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DIMERIZATION AND HYDRATION OF BENZOIC ACID AND SALICYLIC ACID IN APROTIC SOLVENTS

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DIMERIZATION AND HYDRATION OF BENZOIC ACID

AND SALICYLIC ACID IN APROTIC SOLVENTS

APPROVED BY

DISSERTATION COMMITTEE

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Dedicated with love to the memory

of

my father,

Charles Bentley Van Duyne

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CHAPTER I

INTRODUCTION

Molecular association of polar molecules has become a widely accepted concept in chemical bonding theories. The primary goal of the many studies which have dealt with the subject has been to determine the nature of the interactions which hold associated molecular complexes together. Association has most often been attributed to the formation of hydrogen bonds between the polar molecules of the complexes. Although much work has been devoted to the study of the hydrogen bond, many properties of hydrogen bonding systems still remain uncertain (1).

One of the earliest studies of molecular association was conducted by W. Nernst (2) and published in 1891. The distribution technique used by Nernst provided evidence that benzoic acid and salicylic acid formed dimers in

benzene solutions. Dimerization of carboxylic acids by hydrogen bonding has since become widely recognized, and the distribution method has become firmly established as a "classical" method for studying molecular association.

A common error has been made by previous users of the distribution method for determining association constants of polar solutes in organic solvents. In practically all reported studies, the role of dissolved water in the organic medium has been neglected. Erroneous results have been obtained in such cases because hydrates are formed in the nonaqueous solvent due to hydrogen bond formation between water molecules and molecules of the polar solute. The presence of hydrates must be taken into account before reliable results can be gained by the distribution experiment. In fact the distribution experiment is not a sufficient means for studying such systems unless water solubilities in the nonaqueous phase are determined.

Christian, Affsprung, and Taylor (3) have described a more reliable use of the distribution technique. The improved method has been used to study the self-association and hydration of benzoic acid and acetic acid in benzene (4).

Water concentrations in benzene as well as acid concentrations in both phases were determined. Acid hydrate formation in the water-saturated benzene phase was considered in a graphical interpretation of the distribution data. Values of acid dimerization constants calculated from the data were strongly dependent upon the type of hydration assumed in the data fitting process. For example the dimer formation constant for benzoic acid in benzene at 25°C was determined as 2200 l./mole when acid monomer monohydrate formation was assumed. The corresponding value for assumed monomer dihydrate formation was found to be 490 l./mole. Although the data tended to fit the latter assumption somewhat better than the monomer monohydrate assumption, no definite preference was inferred from the distribution data alone. The need for further experimental data for determining reliable association constants was recognized.

Christian, et al. (5) have developed a unique isopiestic technique for studying hydration processes in organic solvents. The isopiestic technique has been combined with distribution measurements to study association processes involving phenol (6), some ketones (7,8) and several amines (9) in organic solvents. Molecular association of benzoic acid and salicylic acid in organic solvents,

studied by Nernst in the original distribution experiments has been studied in the present research by similar techniques supplemented by vapor pressure lowering measurements.

In addition to distribution studies, several different methods have been used to study the association of carboxylic acids (10,11). Results obtained by the various methods have generally shown that carboxylic acids tend to associate in aprotic solvents, with the predominant associated species in dilute solution being the acid dimer. The tendency to associate has usually been determined by measurements of the dimerization constant. Information concerning the structure of the dimer has not been obtained in most studies, but a considerable amount of evidence has indicated that the carboxylic acid dimer in nonpolar solvents is cyclic, particularly in dilute solutions (1,10,12).

Reported studies dealing specifically with the association of benzoic acid and salicylic acid are reviewed briefly in the remainder of this introduction.

Survey of Previous Distribution Studies

Nernst's distribution studies were extended by Hendrixson (13) in 1897. In order to explain the distribution of benzoic acid and salicylic acid between benzene

and water and chloroform and water, Hendrixson assumed that the acids were partially dimerized in the organic solvent and existed entirely as monomers in the aqueous phase. Dimerization constants based on the two assumptions were determined from the data at 10°C and 40°C, and heats of dissociation were calculated. Hydration of the acids in the wet organic solvents was not considered in the data evaluation.

The influence of water in distribution systems was later recognized by de Szyszkowski (14,15) who noted that the solubilities of benzoic, salicylic, and o-nitrobenzoic acids were greater in water-saturated benzene and chloroform than in the partially dry solvents. The estimated degree of hydration of the acids in the organic solvents was found to increase with temperature. The increase in hydration was attributed to increasing solubility of water in the nonaqueous phase with increasing temperature. Cohen and co-workers (16, 17,18) also noted that the solubility of salicylic acid was always less in dry organic solvents than in the solvent containing some amount of water.

An attempt was made in 1927 by von Szyszkowski to study quantitatively the hydration of carboxylic acids in organic solvents using the distribution method (19).

Benzoic acid, salicylic acid, o-nitrobenzoic acid, and m-nitrobenzoic acid were distributed between water and benzene at 25°C. In addition to the acid monomer and dimer species, a hydrated monomer complex was assumed to exist in the water-saturated organic phase. Moreover, acid tetramer formation was postulated for both nitrobenzoic acids. From the acid concentrations in each phase and the solubilities of the acids in water-saturated and dry benzene, equilibrium constants for the various systems were calculated. The definite influence of hydration on the values of the dimer dissociation constants and the monomer distribution constants was demonstrated. Calculation of monomer hydration constants was not attempted due to the lack of accurate water solubility measurements and data concerning the state of association of water in benzene. Values of degree of hydration, defined as the percentage of monomers which were hydrated, as given for each acid were: benzoic(0.575), salicylic (0.494), o-nitrobenzoic (0.573), and m-nitrobenzoic (0.80). The effect of dissolved water on the solubility of the acids in benzene was shown by the values given for the ratio of the difference between acid solubility in dry and water-saturated benzene to the solubility of acid in dry benzene. Values of the relative increase in acid solubility so defined were given in

percentage as: 3.1% (benzoic), 31.2% (salicylic), 60% (o-nitrobenzoic), and 26.7% (m-nitrobenzoic).

Further proof of acid hydration in benzene was found in the distribution of salicylic acid and 1,3,5-dinitrobenzoic acid between benzene and aqueous KCl solutions at 25°C (19,20). The solubilities of the acids in benzene over the salt solutions was smaller than over pure water and decreased with increasing KCl concentration. The acid solubility decrease was correctly explained in terms of hydration and salt concentration; i.e., the solubility of water in benzene decreased with increasing salt activity, and the concentration of hydrated acid complexes decreased accordingly.

Even though the importance of hydration in distribution systems had been established very early in molecular association studies, distribution data continued to be misinterpreted. Very soon after von Szyszkowski's findings, Smith and White (21) studied the distribution of a number of organic acids at 25°C in the systems; water-toluene, water-benzene, and water-chloroform. The data were interpreted on the assumption that acid dimers were the only associated species formed in the nonaqueous phases. Analysis of the data was similar to the graphical treatment used by Hendrixson.

Dimer dissociation constants for benzoic acid in toluene and chloroform were given as 6.33×10^{-3} mole/l. and 12.7×10^{-3} mole/l., respectively. 30.3×10^{-3} mole/l. and 13.2×10^{-3} mole/l. were given as the respective values for salicylic acid in the same solvents, indicating a solvent effect in the opposite direction.

Application of the distribution method to the study of associating substances was discussed in general terms by Almquist (22). Taking A and A_n to represent single and associated molecules in the y-phase, respectively, and A' and A_n' to represent single and associated molecules in the x-phase, respectively, the equilibrium and corresponding constants were considered to be:

$$nA \rightleftarrows A_n \qquad K_1 = (A_n)/(A)^n \tag{1}$$

$$A \rightleftarrows A' \qquad K_2 = (A')/(A) \tag{2}$$

$$nA' \rightleftarrows A_n' \qquad K_3 = (A_n')/(A')^n \ . \tag{3}$$

The total concentrations of the associating substance in the two phases were given by:

$$C_x = n(A_n') + (A') \tag{4}$$

and

$$C_y = n(A_n) + (A) \ . \tag{5}$$

In terms of (A) and the equilibrium constants, C_x and C_y were expressed as

$$C_x = nK_3K_2^n(A)^n + K_2(A) \quad (6)$$

$$C_y = nK_1(A)^n + (A) \quad . \quad (7)$$

When the y-phase was taken to be water, the term, $nK_1(A)^n$, was considered negligible since no association in water was likely. For cases involving water as one phase of the system, the distribution ratio was therefore given by

$$C_x/C_w = nK_3K_2^n(C_w)^{n-1} + K_2 \quad (8)$$

where C_w represented the nondissociated monomer concentration in water. Application of equation 8 to distribution data for several carboxylic acids found the distribution ratio to be linear with C_w indicating that n was 2. The working equation for carboxylic acids was given as

$$C_x/C_w = 2K_3K_2^2C_w + K_2 \quad . \quad (9)$$

Acid dimerization constants, K_3, and monomer distribution constants, K_2, were calculated from the slopes and intercepts of the distribution data plotted as C_x/C_w versus C_w.

The graphical technique described by Almquist has been commonly used for computing equilibrium constants for carboxylic acids from distribution data. Moelwyn-Hughes (23) used the same method to study acetic acid in the water-benzene system at several temperatures. He also reinterpreted Nernst's data for benzoic acid in benzene at 20°C and obtained

a dimer dissociation constant of 5.7×10^{-3} mole/l.

In the same manner Davies and Griffiths (24) calculated monomer distribution constants and dimer dissociation constants for several substituted benzoic acids in some organic solvents. The point was established that the dissociation constants and dissociation energies calculated for substituted benzoic acids differed somewhat from corresponding values obtained in dry solvents by other methods. From similar comparison for benzoic acid, it was concluded that water saturation of benzene in the distribution experiment had little effect on the calculated value of the dissociation constant.

The distribution of salicylic acid between water and cyclohexane was studied at six temperatures from 24°C to 55°C by Banewicz, Reed, and Levitch (25). Their graphical interpretation differed from that indicated by equation 9. From data at very dilute concentrations, the ionization constant of salicylic acid in water and the monomer distribution constant were calculated on the assumption that acid dimerization in cyclohexane was negligible. The calculated ionization and distribution constants were then used to determine the acid dimerization constant from data at higher concentrations. The apparent heat of dimerization calculated from the variation of the dimerization constant

with temperature was found to be -24.5 kcal/mole, considerably larger than the expected heat of dimerization for carboxylic acids in organic solvents.

Benzoic acid was distributed between water and benzene at seven temperatures from 5°C to 35°C by Huq and Lodhi (26). Monomer distribution constants and dimer dissociation constants were calculated at each temperature from a least squares treatment of the data with regard to equation 9. The standard enthalpy for dissociation of benzoic acid dimers in benzene was found to be 7500 cal/mole. Corresponding values of the dimer dissociation constant, Gibb's free energy and entropy at 25°C were reported as 3.85×10^{-3} mole/l., 3260 cal/mole, and 14.2 cal/mole deg, respectively. The possibility of acid hydration influencing the calculated value of the dimerization constant was discussed, but the influence was considered to be small and no attempt was made to treat hydration quantitatively.

Studies by Other Techniques

Cryoscopic measurements of Peterson and Rodebush (27) indicated that the apparent molecular weights of benzoic acid and acetic acid in benzene solution were greater than the formula weights and increased with increasing concentra-

tion. In a more recent study Barton and Kraus (28) interpreted the freezing point lowering of benzoic acid in dry benzene in terms of monomer-dimer equilibrium and calculated a dimer dissociation constant at 5.4°C equal to 6.4×10^{-4} molal.

Numerous ebullioscopic studies of the association of carboxylic acids have been performed. Wolf and Metzger (29) measured the dimerization constants of several monocarboxylic acids in benzene and cyclohexane at 80°C. Dissociation constants reported for benzoic acid and salicylic acid in benzene were 0.97×10^{-2} molal and 5.6×10^{-2} molal, respectively. Similar measurements indicated that dicarboxylic acids form complexes larger than the dimer. Allen and Caldin (30) determined dimer dissociation constants for benzoic and five other carboxylic acids in benzene at three temperatures from boiling-point measurements. The values given in mole fraction units for benzoic acid were: 13.0×10^{-4} at 80.1°C; 8.04×10^{-4} at 65.4°C; and 5.19×10^{-4} at 53.8°C. The calculated dissociation energy of the benzoic acid dimer was 8.05 kcal/mole.

Wall and co-workers (31,32) measured the dissociation constant of the benzoic acid dimer in benzene by using an isopiestic technique. From results obtained at three tempera-

tures, it was found that the dimer dissociation constant could be represented in molar units by log K = 3.383 - (1841/T). The corresponding heat of dissociation of the dimer was 9000 cal/mole. A different isopiestic technique was used by Harris and Dunlop (33) in a recent attempt to determine the dimerization constant of benzoic acid in benzene. Although the method yielded precise values for the osmotic coefficients of the solutions, it failed to give reliable values for the dimerization constant. Coetzee and Lok (34) used a differential vapor pressure technique to measure dimer association constants of several carboxylic acids in ethylene dichloride solutions at 37°C. The values found for benzoic acid and salicylic acid were 87 l./mole and 15 l./mole, respectively. Bruckenstein and Saito (35) used a similar technique to study the dimerization of a number of carboxylic acids in benzene at 25°C and found the dimerization constants for benzoic acid and salicylic acid to be 500 l./mole and 71 l./mole, respectively.

Pohl, Hobbs, and Gross (36,37) studied the association of several carboxylic acids in benzene and heptane by dielectric measurements. The dimer dissociation constant for benzoic acid in benzene at 30°C was found to be 3.4×10^{-3} mole/l. For the same temperature, Buckingham and Raab (38)

obtained the value 2.9×10^{-2} mole/l. by assuming the benzoic acid dimer to be nonpolar and the value 2.2×10^{-3} mole/l. by assuming a polar dimer. Palm and Dunken (39) used previously determined dimerization constants to calculate monomer and dimer dipole moments for benzoic acid in benzene at four temperatures between 15 and 45°C. The association constants which were used were found in molal units from the expression

$$\log K = (1906/T)-3.62,$$

a result of ebullioscopy, cryoscopy, and infrared spectroscopy (40).

Meier, et al. (41,42,43) studied the rates of association and dissociation of benzoic acid in carbon tetrachloride and toluene by ultrasonic absorption. Specific rate constants and dimerization constants were calculated over the temperature range 10-55°C. Values found for the dimer dissociation constant at 25°C were 1.5×10^{-4} mole/l. in carbon tetrachloride and 2.3×10^{-3} mole/l. in toluene. Corresponding heats of dissociation were given as 10.4 kcal/mole in carbon tetrachloride and 5.8 kcal/mole in toluene. Acoustic absorption was also used by Rassing, Osterberg, and Bak (44) to study the association of benzoic acid and some para substituted derivatives of benzoic

acid in dimethyl formamide at 25°C. The dimer dissociation constant for benzoic acid was reported as 5.3 mole/l.

With the exception of the distribution method, the most common technique for studying association of carboxylic acids has been infrared spectroscopy. The effect of hydrogen bonding on the spectrum of carboxylic acids was discussed long ago by Buswell, Rodebush, and Roy (45) and Davies and Sutherland (46). The latter investigators (47) also examined the integrated intensities of the monomeric O-H and C=O bands as a means of determining dimerization constants for benzoic acid and acetic acid in carbon tetrachloride solutions. Association of benzoic acid in solution has since been studied by several investigators using infrared spectroscopy. Dimerization constants determined in some of these studies have been collected and presented in Table I. Calculation of the dimerization constants from absorption measurements required the assumption of a cyclic dimer containing two hydrogen bonds. Constants were then deducible from the "free" and/or "hydrogen-bonded" bands. Hanrahan and Bruce (52) confined their calculations to data obtained at very dilute concentrations (less than 0.004M) as they believed noncyclic dimers to exist at greater concentrations.

Table I. Dimerization Constants for Benzoic Acid from Infrared Absorption Measurements

t(°C)	Solvent	Concn. Range (mole/l.)	K (l./mole)	Band Intensity Measured	Reference
25	CCl_4	$1x10^{-5}$ - $1x10^{-2}$	14,300	O-H (monomer)	48
24	CCl_4	2 x 10^{-2}	4,420	O-H (monomer)	49
24	CCl_4	$1x10^{-4}$ - $1x10^{-1}$	2,300	C=O (monomer and dimer)	50
24	$CHCl_3$	$1x10^{-4}$ - $1x10^{-1}$	400		
35	c-C_6H_{12}	$1x10^{-3}$ - $1x10^{-2}$	5,830	C=O (monomer and dimer)	51
48			2,250		
60			1,210		
30	CCl_4	$2x10^{-4}$ - $2x10^{-2}$	3,660		
45			1,560		
60			710		
30	C_6H_6	$2x10^{-3}$ - $1x10^{-1}$	462		
38			359		
45			269		
60			150		
25	CCl_4	$1x10^{-4}$ - $4x10^{-3}$	5,640	C=O (monomer and dimer)	52
45			2,350		

Forbes, et al. (53,54,55) determined the ultraviolet absorption spectra of several substituted benzoic acids in cyclohexane solution. For each acid a concentration dependence was observed for the main absorption band located in the 225-250 mμ region which was attributed to the effect of dilution on acid monomer-dimer equilibrium. Evaluation of molar absorbtivities for the monomer and dimer species was considered impossible, hence dimerization constants were not calculated. Comparison of the concentration effect for the various acids indicated that m-methyl, p-methyl, and p-hydroxy substitution strengthened the dimeric hydrogen bond, whereas o-methyl, o-hydroxy, and o-methoxy substitution weakened the dimeric hydrogen bond. The behavior of the ortho-substituted acids were attributed to intramolecular hydrogen bonding. Hosoya, Tanaka, and Nagakura (56) observed the same concentration dependence for the 230 mμ band of benzoic acid in n-heptane and calculated a dimer formation constant of 7.95×10^3 l./mole at 30°C. In a similar study, Ito (57) used the concentration dependence of the 280 mμ band of benzoic acid in n-hexane to compute a dimerization constant of 1.76×10^4 l./mole at room temperature.

Nuclear magnetic resonance spectroscopy has been applied to the study of benzoic acid dissolved in benzene. After attempts to determine the dimerization constant failed, Davis and Pitzer (58) explained measured chemical shifts at several temperatures by assuming the dimerization constant to be 5.25×10^3 (mole fraction units) at 30°C, and the association energy to be -8.4 kcal/mole. Association of the acid monomer with benzene was suggested to explain the exceptionally high values calculated for the monomer chemical shift. Muller and Hughes (59) re-investigated the dilution shifts of benzoic acid in rigorously dried benzene by the same technique. The chemical shift found for the monomer was much smaller than found by Davis and Pitzer indicating that their value was adversely affected by small amounts of dissolved water.

The hydration of benzoic acid in diphenylmethane at 25°C has been studied recently by Wood, Mueller, Christian, and Affsprung (60). Two types of measurements were used to investigate the system; distribution ratios of benzoic acid between diphenylmethane and 1 mole/l. aqueous sodium benzoate, and vapor pressures of benzoic acid-diphenylmethane solutions containing various amounts of water. Since both benzoic acid and diphenylmethane were nonvolatile, the measured

vapor pressures were simply the partial pressures of water dissolved in the acid solutions. Several choices of hydrated species were assumed in fitting the water solubility, partial pressure, and distribution data. A satisfactory fit of all the data was achieved when the hydrated species were assumed to be the monomer dihydrate and dimer monohydrate. Equilibrium constants calculated for the formation of the associated species from monomers were found to be: 370 ± 10 l./mole for the dimer; 483 ± 21 $l.^2/mole^2$ for the monomer dihydrate; 890 ± 55 $l.^2/mole^2$ for the dimer monohydrate.

Statement of the Problem

Previous studies indicate that dissolved water is involved in the association equilibria of carboxylic acids in organic solvents. Information gained by the numerous methods for studying molecular association has been affected in many cases by residual amounts of water. Hydration is particularly important in distribution systems, because the nonaqueous medium is saturated with water. Molecular association of benzoic acid and salicylic acid has received considerable attention, but few attempts have been made to study quantitatively the hydration of these compounds. The early distribution study by von Szyszkowski (19,20) is noteworthy, but the problem was oversimplified and accurate

water solubility measurements were not obtained. The studies of Christian and co-workers (4,60) involving the association of benzoic acid in benzene and diphenylmethane have clearly demonstrated the importance of hydration. Investigation of the benzoic acid-benzene system has been extended as a part of the present research. In addition, the association properties of salicylic acid were studied in three solvents of varying reactivity; viz., carbon tetrachloride, benzene, and ethylene dichloride.

The objectives of this research were:

1. To determine the manner in which benzoic acid and salicylic acid self-associate in non-aqueous solvents.
2. To examine the hydration processes which occur in the acid solutions containing various amounts of water.
3. To evaluate the equilibrium constants which govern these hydrogen bonding processes.

CHAPTER II

EXPERIMENTAL

General

Reagent A.C.S. benzoic acid (Baker and Adamson) and U.S.P. salicylic acid (Merck) were used without further purification. All solvents were purified by distillation through either a 30-plate Oldershaw column or a 27-plate Ace Glass column. A constant reflux ratio of 10:1 was maintained during the distillation process by a Flexopulse cycle timer which controlled a solenoid-operated valve contained in the column head. Benzene and carbon tetrachloride (both Baker and Adamson, Reagent A.C.S.) were distilled directly, but ethylene dichloride (Eastman, Pure) was scrubbed before distillation. The scrubbing treatment consisted of successive washings of the solvent with concentrated sulfuric acid until no dark coloration could be observed in the acid. The solvent was then washed with a sodium hydroxide solution and last with distilled water.

Excess water was removed with calcium chloride before the ethylene dichloride was finally distilled.

Acid concentrations in both aqueous and nonaqueous solutions were determined by titration with standard sodium hydroxide solutions. End points for all acid titrations were detected with a Beckman Zeromatic pH meter equipped with a glass electrode in combination with a calomel reference electrode. In order to titrate non-aqueous samples, 50 ml. of distilled water were combined with the sample, and the resulting two-phase system was stirred very rapidly with a Sargent bar magnet stirrer. Titrations were performed on duplicate samples of all acid systems so that each concentration was determined by averaging the results of two titrations. In practically every case, end-points for duplicate samples could be reproduced within the limits of the buret readings. A 50 ml. Fischer-Porter Lab Crest buret was used.

The standard alkali solutions were prepared by dissolving appropriate amounts of 50% sodium hydroxide solution (Fischer, Certified Reagent) in previously de-gassed, distilled water (61). The resulting carbonate free solutions were standardized by titrating weighed amounts of dry potassium hydrogen phthalate (Fischer, Primary Standard).

Titers of the standard solutions ranged from 0.01 mole/l. to 0.05 mole/l. depending upon the particular system to be analyzed. Standard solutions were stored in 12 l. bottles which were fitted with two-hole stoppers with a siphon delivery tube in one hole and a soda lime tube in the other.

Water concentrations in the nonaqueous media were measured by Karl Fischer titrations. Titrations were performed automatically by means of a Beckman KF-3 Aquameter. The setting of the instrument's timer control required the unstable end-points to persist for 30 seconds before the titration stopped. Inherent instability of the end points limited the precision of the water determinations. Each titration procedure was exactly duplicated in order to facilitate precision. The desired reproducibility was in this way achieved for identical samples. In all cases water concentrations were determined by averaging the results of at least three titrations on identical samples.

A stock solution of Karl Fischer reagent was prepared by dissolving 30 grams of iodine in 2 pints of pyridine and diluting with 2300 ml. of methanol (6,62). The titrating solution was prepared by adding approximately 60 ml. of sulfur dioxide collected in a dry ice-acetone trap to 1 l. of the stock solution and diluting with methanol. The

amount of methanol added in the dilution depended upon the desired titer strength. After preparation the titrating reagent was sealed in a 2 l. bottle at least 24 hours before use. Titers of Karl Fischer reagent ranged from 0.04 to 0.13 mole/l. as required by a particular organic solvent.

The method adopted for standardizing the Karl Fischer reagent proved to be very reliable as well as convenient. The titer determinations were achieved by titrating the pure solvents saturated with water at 25°C and using previously determined values of water solubility in the various solvents to make the titer calculation. The water solubilities used in the titer determinations were: 0.0087 mole/l. in carbon tetrachloride, 0.0349 mole/l. in benzene, and 0.1262 mole/l. in ethylene dichloride (6). Titers determined in this way agreed very well with those found by titrating weighed amounts of sodium tartrate dihydrate (63). The use of water-saturated, pure solvents for the titer determinations made the results of the water analyses more nearly self-consistent since reagent standardizations were performed in exactly the same manner as the analysis of solutions containing unknown amounts of water.

Distribution and isopiestic samples were thermostated

at 25.00±0.05°C in a constant temperature water bath. The bath was large enough to accommodate all samples of a complete experiment. Temperature control was maintained by an electronic relay (Emil Greiner Co., Model E-2) equipped with a mercury thermoregulator (Precision Thermometer and Instrument Co., Princo Magna Set). This arrangement controlled the heating provided by two 200 watt light bulbs which were coated with black paint. Continuous cooling was accomplished by pumping water from a refrigeration bath maintained at about 15°C through a coil of copper tubing immersed in the temperature controlled bath. Water in the bath was circulated vigorously by two Little Giant Model CP-5000 pumps.

Distribution Experiments

Distributions of the acids between water and the organic solvents were executed in 500 ml. ground glass stoppered Erlenmeyer flasks. In preparing the samples, sufficient volumes of both water and organic solvent were used to allow the necessary sampling of both phases. 175 ml. of distilled water was sufficient in all distribution experiments. The corresponding volumes for organic solvents were: 300 ml. of carbon tetrachloride, 250 ml.

of benzene, and 125 ml. of ethylene dichloride. These volumes reflect the size of samples used for analytical purposes. For instance in water titrations, 50 ml. samples of carbon tetrachloride solutions were required compared to 10 ml. samples of ethylene dichloride solutions.

Flasks containing appropriate amounts of acid dissolved in the two immiscible solvents were shaken vigorously for about 30 seconds and suspended in the constant temperature bath. Shaking was repeated several times during the first few hours to assist the attainment of equilibrium. At least three days were allowed for the distribution samples to equilibrate.

Sampling of the solutions was done with a pipet of the proper size equipped with an Instrumentation Associates Propipette. In order to sample carbon tetrachloride for water titrations a special technique was employed (6). Very thin bulbs were blown on one end of glass tubes which were long enough to reach through the aqueous layer to the denser carbon tetrachloride phase. Approximately 30 minutes after introducing the closed end of a glass tube into the denser phase, the bulb was broken and a pipet was inserted through the tube for sampling. The technique completely eliminated water droplet contamination of the

sample.

Controlled Water Activity Experiments

Water activities in the nonaqueous solvents were controlled in a series of experiments conducted in isopiestic apparatuses. With the exception of the seal, the isopiestic equilibration cells were almost identical to those described previously (5). The cells were one quart Mason jars with glass tubes taped to their sides. When the cells were placed in the constant temperature bath, the glass tubes were fitted around metal rodes mounted vertically in the bath. This arrangement allowed the system to float in the vigorously stirred bath which agitated the contents of the cell. In addition to the nonaqueous solutions of interest, the equilibration cells contained 100 ml. beakers of constant water activity solutions. The system contained in a sealed cell reached equilibrium by water transfer through the vapor phase from the aqueous solution in the beaker to the nonaqueous solution.

The lids of the isopiestic cells were uniquely constructed for convenient sealing. The seals of the original Mason lids were removed, and the lids were thoroughly

cleaned with acetone. After a hole approximately 1½ cm. in diameter had been drilled through the lid, the inside of the lid was coated with polyethylene. The coating was especially thick (about ½ cm.) over the hole in the lid. A small hole was drilled through the thick polyethylene coating covering the original hole and fitted with a ground glass stopper (₹ 9). The specially constructed lids provided excellent sealing of the cells and also made sampling very convenient. Sampling was accomplished by removing the glass stoppers and pipetting through the small holes. Replacement of the stoppers resealed the cells, and the equilibrium disturbance was held to a minimum.

Constant water activity in the isopiestic cell was maintained by aqueous solutions of either sulfuric acid or calcium chloride. Both types of water activity solutions appeared equally suitable for the application. The choice was limited to sulfuric acid solutions below about 0.2 water activity which is the lower limit obtainable with calcium chloride. Zero water activity was attained by adding phosphorus pentoxide to the small beaker. Water activities of the sulfuric acid and calcium chloride solutions were determined from density measurements and

appropriate data (64,65). Accurate density measurements were obtained with a density balance calibrated with distilled water at 25°C. Because of the small amounts of water transferred from the water source to the organic solvent during equilibration, the water activity of the source did indeed remain constant during the process.

Two different types of experiments were conducted with the isopiestic cells. One type involved measuring increasing water solubility at a given water activity as a function of increasing acid concentration. In such experiments 150 ml. solutions of acid in the organic solvents, ranging in concentration from zero to approximately saturated, were equilibrated at a specific water activity less than 1.0. At least three days were allowed for the establishment of equilibrium; a process which actually should have required less than 10 hours for benzene solutions (5). Acid concentrations and water solubilities at equilibrium were determined by titration of the nonaqueous solutions. Such data were obtained for each of the four systems studied at three distinct values of reduced water activity.

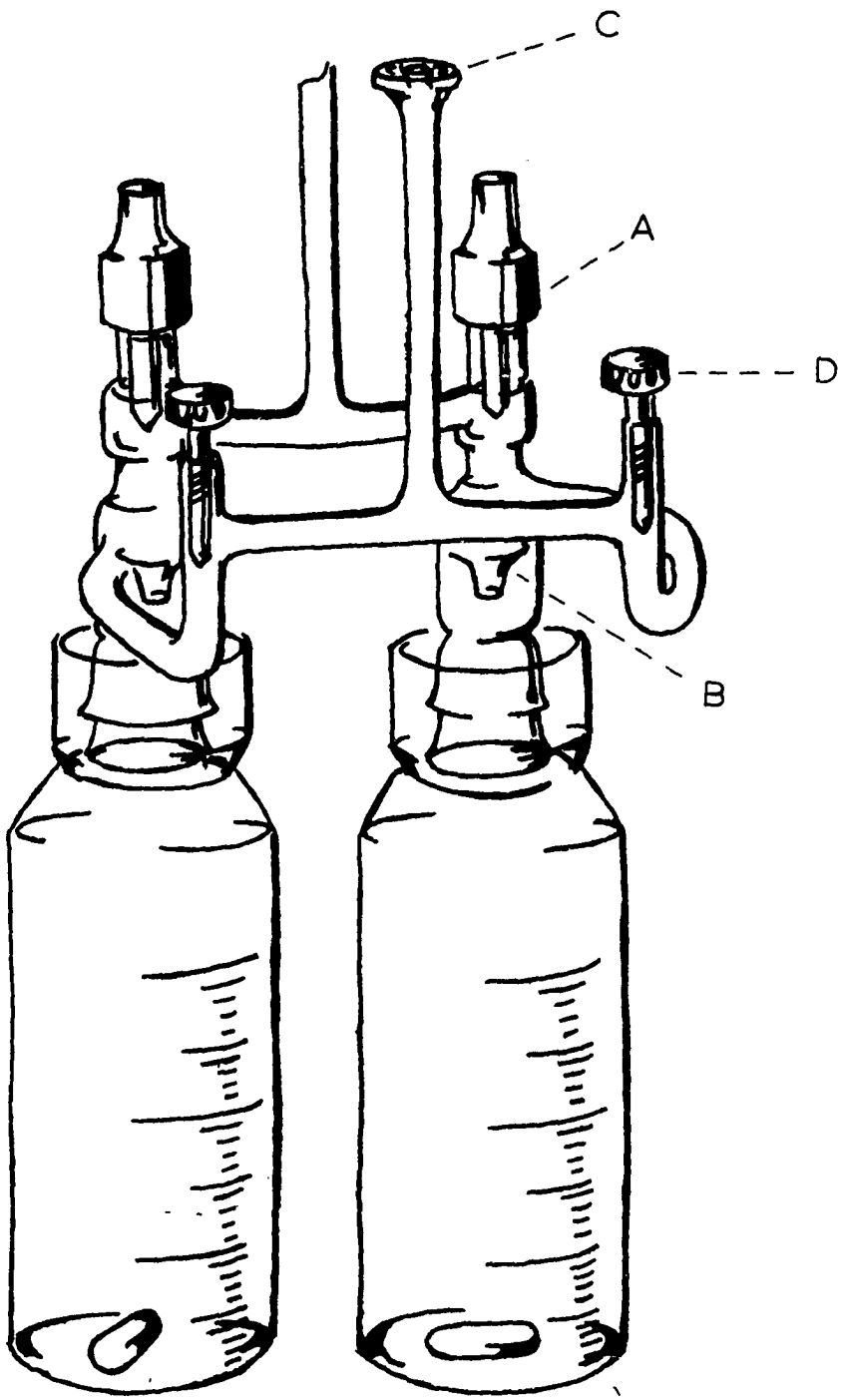
The other use of the isopiestic apparatus was the study of salicylic acid solubility in benzene and in ethylene dichloride when the solvents contained various

amounts of water. 2 l. of the solvent were warmed to about 40°C and saturated with salicylic acid. The solution was divided into 200 ml. aliquots which were equilibrated at 25°C at water activities from 0.0 to 1.0. Since the excess acid apparently crystalized out very slowly during the equilibration process, four weeks were allowed before the solutions were analyzed for acid and water. Results of analyses at six weeks were consistent with the first analyses. Sampling of the saturated solutions was no problem because excess acid was present as large crystals which adhered to the sides of the equilibration cell.

Vapor Pressure Lowering Experiments

The apparatus illustrated in Figure 1 was used in the vapor pressure lowering experiments. It consisted of two cylindrical flasks fitted with a manifold which allowed evacuation of the system and provided linkage to the vapor pressure measuring device. The flasks and manifold were connected by ℸ 24/40 ground glass joints enclosed in cups which held mercury for sealing purposes. Teflon sleeves were used to prevent the joints from freezing when the system was evacuated. The flasks were constructed from a 500 ml. graduated cylinder. Each graduated flask had a

Figure I. Vapor Pressure Lowering Apparatus.



useable volume of approximately 200 ml.

The system was connected to a vacuum line through two DM-850 Delmar-Urry needle valve stopcocks located in the manifold (designated by A in Figure 1). During evacuation of the system, splashing of solutions in the flasks was confined to the lower part of the apparatus by two baffles in the lower part of the manifold (B in Figure 1).

Absolute pressure was determined for each side of the system individually by a Texas Instrument Precision Pressure Gage. The gage was a Model 141 equipped with a Type 1 Bourdon Tube No. 14 Capsule which operated over a pressure range of 0-300 mm of Hg with a minimum resolution of 0.003 mm of Hg. The capsule was connected to both the reference and system lines by means of Gyrolok flareless tube fittings with teflon ferrules. A Welch 1405-H vacuum pump evacuated the reference side of the pressure gage capsule.

Connection of the system to the pressure gage was provided by a 1 mm I.D. capillary in series with a length of glass tubing approximately 2 mm I.D. which was coiled in a spiral. The spiral in the connecting line gave flexibility to the all-glass arrangement. A DM-830 Delmar-Urry o-ring joint (C in Figure 1) connected the capillary to the manifold. Two 795-500 Fischer-Porter 1¼ mm teflon needle

valves (D in Figure 1) opened and closed the two sides of the system to the pressure gage.

Temperature control for the vapor pressure lowering experiments was accomplished by immersing the two flasks containing pure solvent and acid solution into a thermostated water bath. A glass aquarium served as the constant temperature bath which made external viewing of the apparatus possible. Temperature in the bath was maintained at $25.000 \pm 0.002^{\circ}C$ by a Sargent Model ST Thermonitor. The bath heater was a 200 watt light bulb covered with aluminum foil. Cooling was provided by water from a refrigeration bath as described previously. Two Little Giant Model CP-5000 pumps were mounted in the bath in a manner to provide maximum stirring.

The very precise temperature control was necessary for the experiment since even slight temperature fluctuations produced significant changes in the measured vapor pressures. To reduce temperature errors the apparatus was constructed so that the two solution flasks were as close together as possible. No temperature difference between the positions of the two flasks in the bath could be detected by a very sensitive Brooklyn thermometer which could be read to the nearest one or two thousandths of a degree.

In order to prevent condensation of the solvent in regions of the system not contained in the constant temperature bath, a 250 watt infrared heat lamp was suspended about 2 ft. above the experimental apparatus. Temperature in the vicinity of the manifold and gage connecting line were therefore five to ten degrees higher than in the bath.

The vapor pressure lowering experiment was conducted by filling one flask of the apparatus with pure solvent and one with a dilute acid solution of known concentration. Air and water were removed from pure solvent and solution by evacuating through the Delmar-Urry valves. Vigorous stirring was provided by two bar magnet stirrers. Solvent removed in the degassing process was collected in a trap. The amount of solvent which had to be pumped out of the system before degassing was complete depended upon the solvent. The carbon tetrachloride and benzene systems appeared to be completely degassed after removal of about 25% of the total volume of solvent which was consistent with the findings of Mueller (66). Removal of approximately 35% of the total volume of ethylene dichloride was required.

After the degassing process was completed, all valves were closed, and the two separated systems were allowed to reach temperature and pressure equilibrium which required

less than ten minutes for moderate stirring. During the period of equilibrium attainment, the acid residue on the sides of the solution flask was washed down into the solution. An external magnet was used to pull the stirring bar in the flask up and down the sides to produce the washing. The washing procedure was necessary because acid residue on the flask above the solution was found to decrease the measured vapor pressure of the solution. The decrease, which was not reproducible, was apparently caused by absorption of the solvent vapor on the acid residue.

Exactly fifteen minutes after evacuation the vapor pressure of the acid solution was measured by opening the appropriate Fischer-Porter valve. Vapor pressure of the pure solvent was measured in the same manner, and the vapor pressure lowering for the dilute acid solution was then computed from the difference in the two measured pressures.

Results for progressively more concentrated acid solutions were obtained by successive removals of additional solvent from both sides of the apparatus. All procedures were repeated in exactly the same way throughout the experiment. As the experiment proceeded, the volumes of solution and pure solvent were kept approximately equal. The volume adjustment served the dual purpose of minimizing

the increasingly adverse effect of impurities and giving a comparison of solution and solvent vapor pressures under exactly the same conditions.

The original solution was analyzed for acid before filling the apparatus. From the known concentration and the volume of solution at the beginning of the experiment, the amount of acid contained in the solution flask was determined. Titration of the acid remaining after completion of the experiment indicated that the total amount of non-volatile acid did not vary as solvent was removed from the solution. Therefore, it was possible to determine the concentration of the acid solution at all intermediate stages of the experiment by simply measuring the volume of the solution. In order to obtain accurate concentrations, it was necessary to calibrate the solution flask.

To calibrate the solution flask, pure solvent was added to the flask from a previously calibrated 25 ml. pipet. The exact flask reading corresponding to the meniscus of the solvent was determined after each addition by interpolating between graduations on the flask. Relative separations between meniscus and flask markings were determined very accurately with a Gaertner cathetometer. The

volume of acid solution at all points of the experiment was determined from cathetometer readings and the calibration data. The determined volumes were sufficiently accurate to yield acid concentrations with an estimated uncertainty of ±2%.

CHAPTER III

RESULTS AND DATA INTERPRETATION

The Distribution Experiments

The distribution method consists of dissolving various amounts of a particular solute in a system of two immiscible solvents. At equilibrium, the distribution of the solute, A, between the two solvents, a and b, can be denoted by

$$A \text{ (in solvent a)} \rightleftarrows A \text{ (in solvent b)}.$$

The chemical potential of the solute must be the same in each phase under equilibrium conditions. This implies that the fugacity, f_A, is also the same in each solvent;

$$f_A^a = f_A^b \tag{10}$$

where the superscript denotes the solvent. For sufficiently dilute solutions, Henry's law is obeyed by the solute in each phase of the system (67) so that

$$f_A^a = k_A^a \, C_A^a \tag{11}$$

and

$$f_A^b = k_A^b \, C_A^b \tag{12}$$

where C_A is the molarity of the solute and k_A is the corresponding Henry's law constant. Therefore, the distribution law is given as

$$C_A^b/C_A^a = k_A^a/k_A^b = K. \quad (13)$$

The ratio of concentrations necessary to produce equal fugacities of the solute in the two solvents is given by the distribution constant, K.

Association or dissociation of the solute in one or both phases causes apparent deviations from the distribution law. Evidence concerning the nature of the disturbing processes can be obtained by measuring deviations from the distribution law over a range of total solute concentration. For very simple systems, equilibrium constants for the association and/or dissociation reactions can be determined by properly relating the distribution data.

Distribution ratios which have been determined in this research indicate that benzoic acid and salicylic acid associate in the organic solvents. Water solubility in the nonaqueous phase increases as the acid concentration increases which suggests that acid hydrates are formed. Moreover, the distribution data indicate that hydrates of both the acid monomer and dimer are produced in the nonaqueous solvents.

The data may be explained by assuming that the hydrated species existing in the nonaqueous phase are the monomer monohydrate (AW), the monomer dihydrate (AW_2), and the dimer monohydrate (A_2W), and that anhydrous species are the acid monomer (A) and dimer (A_2). Moreover, the acid monomer and the acid anion are assumed to be the only acid species present in the aqueous phase. If the distribution law applies to the acid monomer, and each of the species obeys Henry's law, the distribution of acid between the two immiscible solvents and the association of acid in the nonaqueous phase can be described by the following reactions and corresponding equilibrium constants:

$$A\ (\text{aqueous}) \rightleftarrows A\ (\text{nonaqueous}) \qquad K_D = C_A/C_A^W \qquad (14)$$

$$A + A \rightleftarrows A_2 \qquad K_{20} = C_{A_2}/C_A^2 \qquad (15)$$

$$A + W \rightleftarrows AW \qquad K_{11} = C_{AW}/C_A C_W \qquad (16)$$

$$A + 2W \rightleftarrows AW_2 \qquad K_{12} = C_{AW_2}/C_A C_W^2 \qquad (17)$$

$$2A + W \rightleftarrows A_2W \qquad K_{21} = C_{A_2W}/C_A^2 C_W \qquad (18)$$

where W represents the water monomer, and C denotes molar concentrations. Symbols for the association constants are distinguished by two subscript numbers to specify the formation of a particular associated species from monomers of acid and water. The first subscript specifies the number of acid units in the associated species; the second subscript

gives the number of water units. K_D is the monomer distribution constant.

If the proposed acid species are the correct ones, the total concentration of acid in the nonaqueous phase (as determined by titration analysis) should be given by

$$f_A = C_A + 2C_{A_2} + C_{AW} + C_{AW_2} + 2C_{A_2W} . \quad (19)$$

By combining equations 14 through 19, the total acid concentration can be expressed in terms involving only the equilibrium constants, the water monomer concentration in the nonaqueous phase, C_W, and the acid monomer concentration in the aqueous phase, C_A^W;

$$f_A = K_D C_A^W + 2K_{20}K_D^2 C_A^{W^2} + K_{11}K_D C_A^W C_W +$$

$$K_{12}K_D C_A^W C_W^2 + 2K_{21}K_D^2 C_A^{W^2} C_W . \quad (20)$$

Collecting terms containing equal powers of C_A^W yields

$$f_A = K_D(1 + K_{11}C_W + K_{12}C_W^2)\ C_A^W + K_D^2\ (2K_{20} + 2K_{21}C_W)\ C_A^{W^2} \quad (21)$$

Dividing throughout the equation by C_A^W gives

$$f_A/C_A^W = K_D(1 + K_{11}C_W + K_{12}C_W^2) + K_D^2(2K_{20} + 2K_{21}C_W)\ C_A^W . \quad (22)$$

Accordingly, the distribution ratio, f_A/C_A^W, should be linear with respect to C_A^W, and both are measurable quantities.

A correction for ionization of the acids must be made

in determining C_A^W which is equal to the total acid concentration in water, f_A^W, minus the concentration of the acid anion, C_{A^-}. In making the correction, approximate values of C_{A^-} calculated from a particular value of f_A^W and the thermodynamic ionization constant, K_a^o, have been used to calculate values of the mean ionic activity coefficient from an extended Debye - Hückel equation (68),

$$\log \gamma_{\pm} = -0.5115 \sqrt{C_{A^-}}/(1+ \sqrt{C_{A^-}}) + 0.1C_{A^-} . \qquad (23)$$

Assuming the activity coefficient of the nonionized acid to be unity, the approximate value of the ionization constant at the concentration, f_A^W, is then given by

$$K_a = K_a^o/\gamma_{\pm}^2. \qquad (24)$$

Successive calculations eventually produce the actual value of K_a from which the true value of C_{A^-} can be determined. Values of K_a^o which have been used in ionization corrections are 6.28×10^{-5} mole/l. for benzoic acid (69) and 1.01×10^{-3} mole/l. for salicylic acid (70).

Dissolved water involved in the association equilibria of the system is accounted for by the expression,

$$\Delta f_W = C_{AW} + 2C_{AW_2} + C_{A_2W}. \qquad (25)$$

Δf_W represents the extra amount of water dissolved in the nonaqueous phase as a result of hydration of the acid. Values of Δf_W are determined by subtracting the solubility

of water in the pure solvent from the total solubility of water in the nonaqueous phase of the distribution samples. In terms of equilibrium constants, C_W, and C_A^W equation 25 becomes

$$\Delta f_W/C_A^W = K_D(K_{11}C_W + 2K_{12}C_W^2) + K_D^2K_{21}C_WC_A^W \quad . \qquad (26)$$

Subtracting equation 26 from 22 yields

$$(f_A - \Delta f_W)/C_A^W = K_D(1 - K_{12}C_W^2) + K_D^2(2K_{20} + K_{21}C_W)\ C_A^W \quad . \qquad (27)$$

This equation predicts that the observable value of $(f_A - \Delta f_W)/C_A^W$ also varies linearly with respect to C_A^W.

Christian, Affsprung, and Taylor (3) have discussed the use of equations of types 22 and 27 in the analysis of distribution data. They emphasize the fact that equations in the form of 22, but without the hydration terms, are identical to the expression which has been commonly used in the past for determining distribution and dimerization constants without regard to dissolved water (equation 9 in Chapter I). The point is that distribution data plotted as f_A/C_A^W versus C_A^W will always give linear plots providing no associated species containing more than two acid molecules exists in the system. Equilibrium constants based upon the slope and intercept of such plots are in error if hydration of the polar solute occurs in the nonaqueous medium.

The distribution data for the benzoic acid-benzene-water

system are presented in Table II. The first three columns contain values of experimentally measured, total molar concentrations of water in the nonaqueous phase, f_W, acid in the nonaqueous, f_A, and acid in the aqueous phase, f_A^W. Column four contains values of C_A^W, the concentration of nonionized acid in water. The remaining two columns give values of the distribution ratios as defined by equations 22 and 27. Tables III, IV, and V present in the same manner the distribution data for salicylic acid between water and the three solvents: carbon tetrachloride, benzene, and ethylene dichloride.

The distribution data for these systems are plotted in Figures II, III, IV, and V in the same order as given in the tables. Figure II includes Taylor's data for the benzoic acid-benzene-water system at 25°C. Table VI contains values of slopes and intercepts of the distribution plots which have been determined by least squares treatment of the data.

An examination of the distribution plots reveals immediately the importance of water solubility measurements in the distribution experiment. As already pointed out, the concentration dependence of the classic distribution ratio, f_A/C_A^W, gives no information at all concerning hydration of

a polar solute in the non-aqueous phase. However, when water solubilities are determined, the data plotted according to Figures II through V provide relevant information concerning all equilibrium processes occuring in the system. The plots for the benzoic acid and salicylic acid systems are linear with positive slopes and intercepts. This indicates that species exist containing both one and two acid units, but that no associated species exists containing more than two acid units. Moreover, the least squares slopes and intercepts given in Table VI are greater in each case for the f_A/C_A^W versus C_A^W plot than the respective values of the $(f_A - \Delta f_W)/C_A^W$ versus C_A^W plot. This implies that both monomer and dimer of the acid form hydrates in the nonaqueous solvent. These observations are consistent with the species which have been proposed and the formulation of equations 22 and 27.

Water Solubilities by Varying Water Activity

Although the distribution data suggest quite clearly that both monomer and dimer of the acids exist as anhydrous and hydrated species in the organic solvents, the identity of the specific hydrated species cannot be deduced from such data alone. For instance, if a different set of species involving only acid monomer and dimer and both monomer and

dimer hydrates had been postulated, equations analogous to 22 and 27 would also predict linear distribution plots. Furthermore, the new equations would again predict a greater slope and intercept for f_A/C_A^W versus C_A^W than for $(f_A - \Delta f_W)/C_A^W$ versus C_A^W. Additional data are needed if the hydrated species are to be uniquely determined.

A technique has been developed by Christian and co-workers which allows the measurement of water solubilities in nonaqueous systems at various water activities (5,6). The molecular complexity of water in several organic solvents in the absence of other polar solutes has been studied by this solute isopiestic method (6,71,72,73). The studies indicate that water is primarily monomeric in carbon tetrachloride and benzene but associates significantly in ethylene dichloride. The water solubility-activity data in ethylene dichloride can be adequately explained in terms of monomer-trimer equilibrium.

Assuming the presence of the acid hydrates, the water monomer, W, and trimer, W_3 (for ethylene dichloride only), the solubility of water in a nonaqueous acid solution at a given water activity is given by

$$f_W = C_W + 3C_{W_3} + C_{AW} + 2C_{AW_2} + C_{A_2W}. \qquad (28)$$

Solving for Δf_W, the amount of water "bound" in the form of hydrates, and expressing concentrations of hydrated species in terms of their formation constants gives

$$\Delta f_W = f_W - (C_W + 3C_{W_3}) =$$
$$K_{11}C_A C_W + 2K_{12}C_A C_W^2 + K_{21}C_A^2 C_W. \quad (29)$$

The water monomer concentration, C_W, can be determined from the relationship,

$$C_W = a_W C_W^o \quad (30)$$

where C_W^o is a constant for a particular solvent at a given temperature and a_W is the value of the water activity. Values of C_W^o for the three solvents in this study have been determined from previous experiments. For benzene and carbon tetrachloride at 25°C, the values of C_W^o are 0.0349 mole/l. (6,71) and 0.0087 mole/l. (6,72), respectively. Since water is primarily monomeric in both these solvents, the values of C_W^o may simply be taken as the solubilities of water in the pure solvents at unit water activity. The value of C_W^o for ethylene dichloride at 25°C has been taken as 0.1083 mole/l. (6,73).

Equation 30 allows Δf_W to be expressed in terms of water activity and the constant, C_W^o;

$$\Delta f_W = K_{11} a_W C_W^o C_A + 2K_{12} a_W^2 C_W^{o2} C_A + K_{21} a_W C_W^o C_A^2. \quad (31)$$

The total acid concentration may be expressed in terms of the same variables as

$$f_A = C_A + K_{11} a_W C_W^o C_A + K_{12} a_W^2 C_W^{o2} C_A + 2K_{20} C_A^2 + 2K_{21} a_W C_W^o C_A^2 . \quad (32)$$

Equations 31 and 32 are useful for testing the validity of the proposed hydrate species. If a reasonable set of equilibrium constants can be determined for the formation of the associated species, equation 32 allows the acid monomer concentration, C_A, to be calculated for every combination of f_A and a_W. The calculated value of C_A together with equation 31 allows calculation of a corresponding value of Δf_W. Comparison of calculated values of Δf_W with experimental values for all water activities provides a critical test of the proposed species.

Tables VII, VIII, IX, and X contain water solubilities in the organic solvents, f_W, for various values of water activity, a_W, and concentrations of the acids, f_A. The water solubility data for the four systems are plotted in Figures VI, VII, VIII, and IX. Total acid concentration, f_A, is plotted against total water concentration, f_W. In

each case distinct curves are defined by points corresponding to the same water activity. For the three salicylic acid systems, the highest acid concentration at each water activity represents the acid solubility limit.

Water and Acid Solubility as a Function of Water Activity

An additional type of data has been obtained for two of the systems studied. The solubility of salicylic acid in benzene and in ethylene dichloride increases significantly with increasing water activity. The magnitude of the change in acid solubility in going from the dry solvent to water-saturated solvent at unit water activity is in a range which is convenient to relate to the stoichiometry of the equilibrium processes. Therefore, the solubility of salicylic acid has been measured in benzene and in ethylene dichloride as a function of water activity.

The increase in acid solubility with water activity is a result of the formation of hydrated acid species so that

$$\Delta f_A = f_A - (C_A + 2C_{A_2}) = C_{AW} + C_{AW_2} + 2C_{A_2W}. \qquad (33)$$

The hydrated acid, Δf_A, is a measurable quantity equal to the acid solubility in the solvent at a particular water activity minus the acid solubility in the dry solvent. In

terms of hydration constants and monomer concentrations, equation 33 becomes

$$\Delta f_A = K_{11}C_AC_W + K_{12}C_AC_W^2 + 2K_{21}C_A^2C_W. \quad (34)$$

Collecting terms with equal powers of C_W and dividing throughout by C_W gives

$$\Delta f_A/C_W = (K_{11}C_A + 2K_{21}C_A^2) + K_{12}C_AC_W. \quad (35)$$

The increase in water solubility due to acid hydration can be written in an analogous form.

$$\Delta f_W/C_W = (K_{11}C_A + K_{21}C_A^2) + 2K_{12}C_AC_W. \quad (36)$$

Δf_W may also be determined at each water activity by subtracting the solubility of water in the pure solvent from the water solubility in acid-saturated solvent. C_W is calculated according to equation 30 from the water activity and the appropriate value of C_W^o.

Table XI gives solubilities of water and salicylic acid in benzene at 25°C for several different values of water activity. Table XII contains the same data for salicylic acid in ethylene dichloride. Figures X and XI present the data as plots of $\Delta f_A/C_W$ and $\Delta f_W/C_W$ versus C_W.

Data of acid solubility as a function of water activity have not been obtained for salicylic acid in carbon tetrachloride or for benzoic acid in benzene. The increase in acid solubility over the entire water activity range for

the former system is not significant enough to allow meaningful data analysis. On the other hand, the solubility of benzoic acid in benzene is too great to allow the experiment to be conducted in the necessary region of dilute concentrations.

Determination of Equilibrium Parameters

Equilibrium constants for each acid system have been determined by nonlinear least squares analysis of the distribution and solubility data. Basically, the technique employs a numerical optimum seeking method (74) to minimize the expression,

$$S^2 = W_R \sum \left[(f_A/C_A^W)\text{exptl.} - (f_A/C_A^W)\text{calcd.} \right]^2 + W_w \sum \left[(\Delta f_w)\text{exptl.} - (\Delta f_w)\ \text{calcd.} \right]^2 + W_A \sum \left[(\Delta f_A)\text{exptl.} - (\Delta f_A)\ \text{calcd.} \right]^2 , \quad (37)$$

with respect to the equilibrium constants which are treated as adjustable parameters in the process. Each term in equation 37 defines the sum of the weighted squares of deviations between observed values of a particular variable and values calculated from the adjustable equilibrium constants. For instance, a value of the distribution ratio, f_A/C_A^W, can be calculated from equation 22 for each measured

value of C_A^W and a trial set of equilibrium constants, K_{20}, K_{11}, K_{12}, K_{21}, and K_D ($C_W = C_W^o$ when $a_W = 1.0$). In order to obtain calculated values of Δf_W and Δf_A, the concentration of the acid monomer, C_A, is first calculated from equation 32 for each measured value of f_A, the corresponding value of a_W, and the trial set of equilibrium constants. The calculated values of C_A, values of C_W calculated from equation 30, and the set of hydration constants are then substituted into equation 29 to calculate values of Δf_W and into equation 34 to calculate values of Δf_A. The weight factors in equation 37, W_R, W_w, and W_A are determined from observed uncertainties in distribution ratios, water solubility measurements, and acid solubility measurements, respectively. The calculations and systematic search for the set of equilibrium constants yielding the absolute minimum in S^2 are made possible by use of a digital computer.

Standard errors in the least squares set of equilibrium constants for each system have been calculated by the computer method described by Christian (75) and Sillén (76).

Equilibrium constants obtained by the least squares data analysis for the benzoic acid-benzene-water system are presented in Table XIII. Distribution and water solubility data for the system have been analyzed in two ways. For

method A, a value for the dimerization constant, K_{20}, at 25°C has been determined by extrapolating the results obtained by Allen, Watkinson, and Webb (51) from infrared spectroscopy. This value, 589 l./mole, has been assumed to be correct and held constant in the least squares analysis, thereby reducing by one the number of parameters necessary in fitting the distribution and water solubility data. In method B, all equilibrium constants including the dimerization constant have been treated as adjustable parameters in the least squares data fitting process. Results obtained by both methods are given in Table XIII. In addition to the least squares equilibrium constants, the table gives standard errors in the constants and root-mean-square deviations in the distribution ratio (S_R) and in water solubility (S_W).

In order to illustrate results of the data fitting process, equilibrium constants obtained for the benzoic acid-benzene-water system have been used to calculate the lines in the distribution plots of Figure II and the water solubility curves of Figure VI. Lines calculated from the results of both method A and method B are shown in the figures. In Figure II, the lines calculated for the f_A/C_A^W versus C_A^W plot are nearly identical for each set of equilibrium constants and are represented by a single line

(method A: slope = 1100, intercept = 1.65; method B: slope = 1095, intercept = 1.70).

Least squares parameters for the three salicylic acid systems are given in Table XIV. In each case all equilibrium constants have been determined from the distribution and solubility data as in method B just discussed. It should be noted that the third term of equation 37 applies only to systems for which acid solubility data are available. Therefore, the least squares treatment for the salicylic acid-benzene-water and salicylic acid-ethylene dichloride-water systems differs slightly from the data treatment for the other systems. Correspondingly, root-mean-square deviations in acid solubility (S_A) are included in the table for the benzene and ethylene dichloride systems. The equilibrium constants in Table XIV for the salicylic acid systems have been used to calculate the lines of the distribution plots of Figures III, IV and V, the water solubility curves of Figures VII, VIII and IX, and the lines in Figures X and XI.

Vapor Pressure Lowering Experiments

It is well known that the presence of a solute in a liquid has a significant effect upon the properties of the liquid, particularly its vapor pressure. The addition of a solute to a solvent causes the vapor pressure of the solvent

to be lowered. For sufficiently dilute solutions, the solvent obeys Raoult's law and the vapor pressure lowering of the solvent (ΔP) is proportional to the solute concentration, i.e.

$$\Delta P = X_2 P_1^{\circ} \tag{38}$$

where X_2 is the mole fraction of the solute species, and P_1° is the vapor pressure of the pure solvent. In terms of the mole numbers of solvent (n_1) and solute (n_2), the pressure differential is given by

$$\Delta P = P_1^{\circ} (n_2/n_1) \ , \tag{39}$$

since $n_1 \gg n_2$ for very dilute solutions. Therefore, if one measures ΔP and P_1° the number of moles of solute can be determined from the relation,

$$n_2 = \Delta P/P_1^{\circ} (V_s/\bar{V}_1) \tag{40}$$

in which V_s is the volume of the solution, and $\bar{V}_1$ is the molar volume of the solvent. Furthermore, the gram molecular weight, M_2, of the solute can be deduced if the number of grams of solute, g_2, is known.

For systems in which the solute species self-associates, application of equation 40 yields the "effective" number of moles of solute, n_2', and the "apparent" molecular weight, M_2', is obtained. Vapor pressure lowering measurements therefore provide a means for studying the self-association

of substances in solution. The technique has been applied in this research to study the benzoic acid and salicylic acid systems. The pressure differential has been determined for each system over a range of total solute concentration by the method described in Chapter II. Since the partial pressure of each acid in solution is insignificant compared to the solvent partial pressure, the solvent partial pressure is assumed to be the same as the observed total pressure. Therefore, the measured pressure differential has been taken as the vapor pressure lowering of the solvent, ΔP.

Table XV contains values of total acid concentration, f_A, vapor pressure of pure solvent, P_1^o, and corresponding pressure differentials, ΔP, for the benzoic acid-benzene system. Also included in the table are values of the apparent acid concentration, f_A', which have been calculated for each set of measurements. In the same manner, the vapor pressure lowering data for salicylic acid in carbon tetrachloride, in benzene, and in ethylene dichloride are presented in Table XVI, Table XVII, and Table XVIII, respectively.

The vapor pressure lowering data for the four systems are plotted in Figures XII, XIII, XIV, and XV as the pressure differential, ΔP, versus the total acid concentration, f_A.

The lines drawn in Figures XII through XV have been calculated from the following relationships:

$$f_A = C_A + 2K_{20}C_A^2, \tag{41}$$

$$f_A' = C_A + K_{20}C_A^2 , \tag{42}$$

and $$\Delta P = P_1^o \bar{V}_1 (n_2/V_s) = P_1^o \bar{V}_1 f_A' . \tag{43}$$

Equations 41 and 42 allow calculation of total acid concentration, f_A, and apparent acid concentration, f_A', for various values of acid monomer concentration, C_A, and an assumed dimerization constant, K_{20}. Corresponding values of the pressure differential, ΔP, are then calculated for each value of f_A' by means of equation 43.

Values which have been used for the vapor pressures of the pure solvents, P_1^o, at 25°C are 95.05 mm Hg for benzene, 113.89 mm Hg for carbon tetrachloride, and 78.74 mm Hg for ethylene dichloride. These values represent averages of the observed values given in the tables. Corresponding values which have been calculated from data given by Weissberger, et al. (77) are: 95.13 mm Hg for benzene, 114.06 mm Hg for carbon tetrachloride, and 84.54 mm Hg for ethylene dichloride. The experimental values of P_1^o for benzene and carbon tetrachloride compare quite well with the calculated values and also with values which have been

measured by Mueller (66); 95.07 mm Hg for benzene and 114.08 mm Hg for carbon tetrachloride. For ethylene dichloride, the measured P_1^o is not in agreement with the value calculated from Weissberger's data but does agree well with 78.90 mm Hg measured by Pearce and Peters (78), and 78.50 mm Hg calculated from data given by Jordan (79).

Molar volumes of the solvents have been calculated from molecular weights and solvent densities. Values which have been taken for the densities at 25°C are: 0.8734 g/cm^3. for benzene (80), 1.5843 g./cm^3. for carbon tetrachloride (80), and 1.2455 g./cm^3. for ethylene dichloride (81).

Table II

Distribution Data for the

Benzoic Acid-Water-Benzene System at 25°C

f_W(M)	f_A(M)	f_A^W(M)	C_A^W(M)	f_A/C_A^W	$(f_A - \Delta f_W)/C_A^W$
0.0402	0.0482	0.0065	0.0059	8.15	7.26
0.0436	0.0990	0.0095	0.0088	11.30	10.31
0.0466	0.1453	0.0116	0.0108	13.50	12.42
0.0493	0.1916	0.0134	0.0125	15.35	14.20
0.0525	0.2434	0.0152	0.0142	17.18	15.94
0.0553	0.2915	0.0166	0.0156	18.72	17.41
0.0578	0.3360	0.0178	0.0168	20.06	18.69

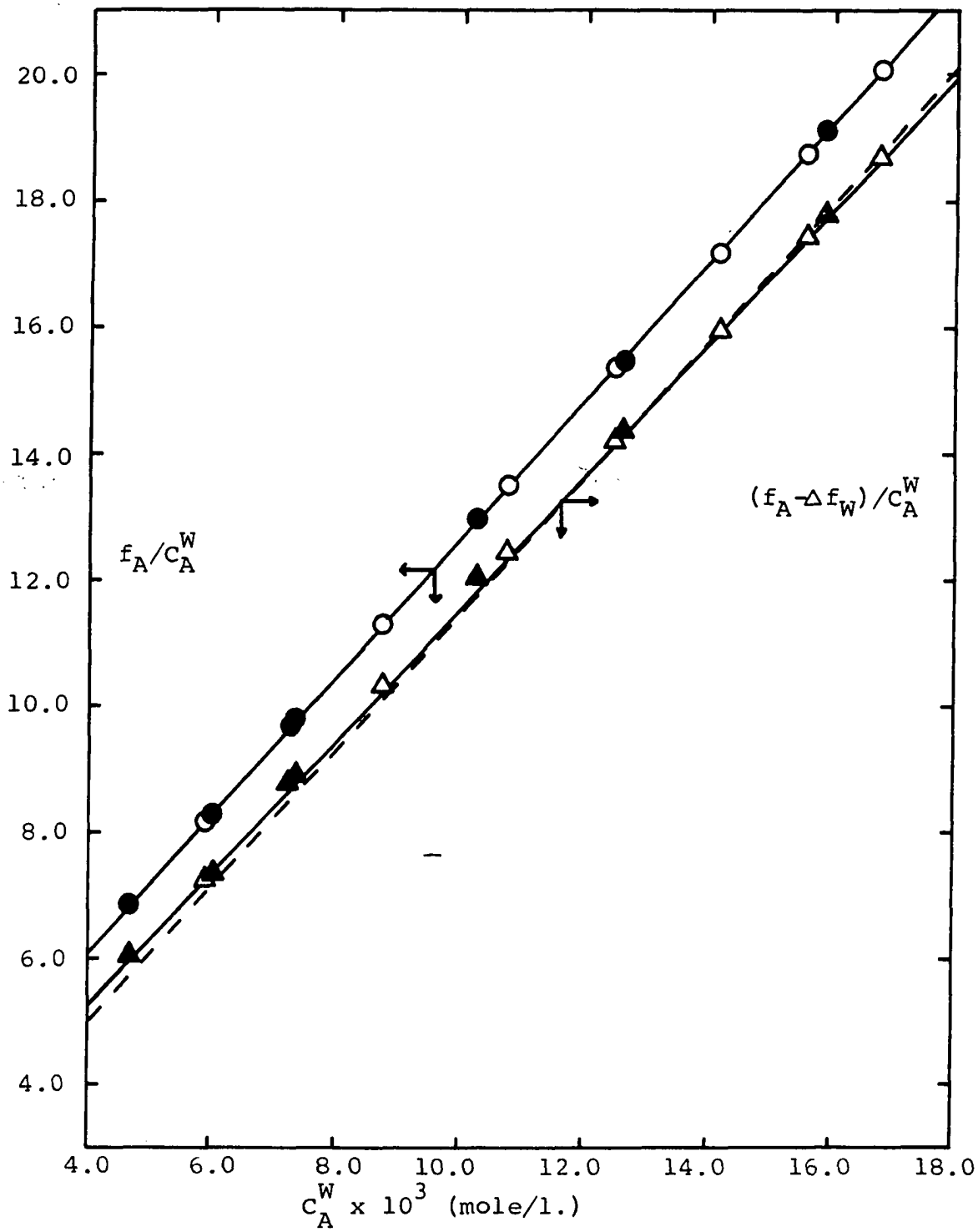


Figure II. Distribution Plots for the Benzoic Acid-Water-Benzene System at 25°C. ● and ▲, Taylor's data (4). Lines are calculated; ----, Method A; ——, Method B.

Table III

Distribution Data for the Salicylic Acid-Water-Carbon Tetrachloride System at 25°C

f_W(M)	f_A(M)	f_A^W(M)	C_A^W(M)	f_A/C_A^W	$(f_A - \Delta f_W)/C_A^W$
0.0088	0.0010	0.0027	0.0015	0.676	0.581
0.0092	0.0026	0.0047	0.0029	0.910	0.722
0.0093	0.0051	0.0066	0.0044	1.160	1.030
0.0097	0.0075	0.0080	0.0055	1.350	1.170
0.0096	0.0098	0.0093	0.0066	1.491	1.362
0.0099	0.0128	0.0106	0.0077	1.662	1.510
0.0101	0.0161	0.0118	0.0087	1.862	1.702
0.0103	0.0199	0.0132	0.0098	2.019	1.860
0.0106	0.0248	0.0146	0.0111	2.241	2.068
0.0109	0.0288	0.0157	0.0120	2.408	2.226

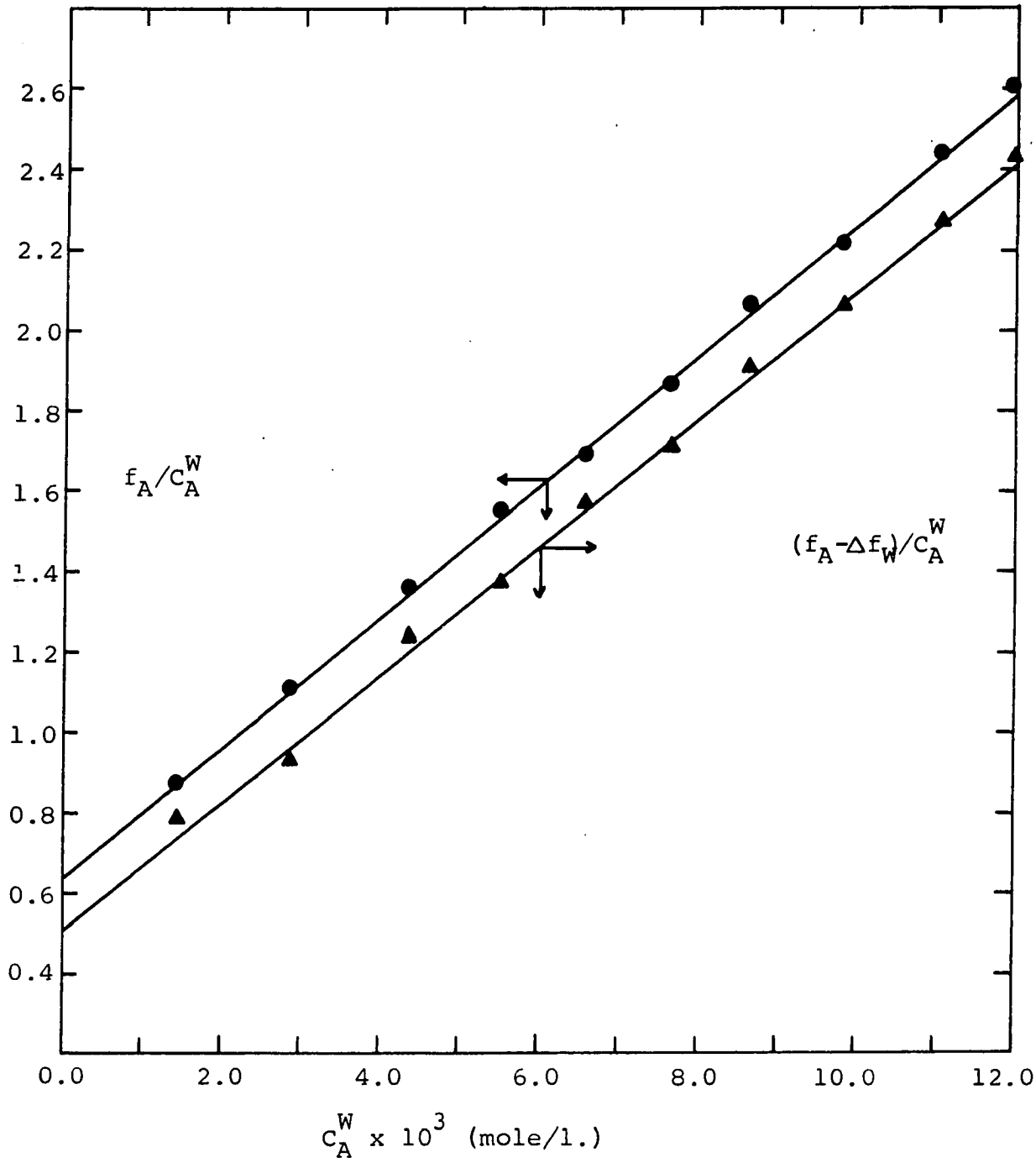


Figure III. Distribution Plots for the Salicylic Acid-Water-Carbon Tetrachloride System at 25°C. Lines are calculated.

Table IV

Distribution Data for the Salicylic Acid-Water-Benzene System at 25°C

f_W(M)	f_A(M)	f_A^W(M)	C_A^W(M)	f_A/C_A^W	$(f_A-\Delta f_W)/C_A^W$
0.0369	0.0041	0.0029	0.0016	2.512	1.275
0.0384	0.0078	0.0045	0.0028	2.809	1.555
0.0403	0.0134	0.0064	0.0043	3.148	1.878
0.0421	0.0195	0.0081	0.0056	3.480	2.196
0.0442	0.0255	0.0096	0.0068	3.749	2.383
0.0462	0.0331	0.0111	0.0081	4.086	2.692
0.0476	0.0394	0.0123	0.0091	4.322	2.929
0.0504	0.0510	0.0143	0.0108	4.746	3.304
0.0529	0.0634	0.0161	0.0124	5.132	3.675
0.0530	0.0625	0.0160	0.0123	5.089	3.615

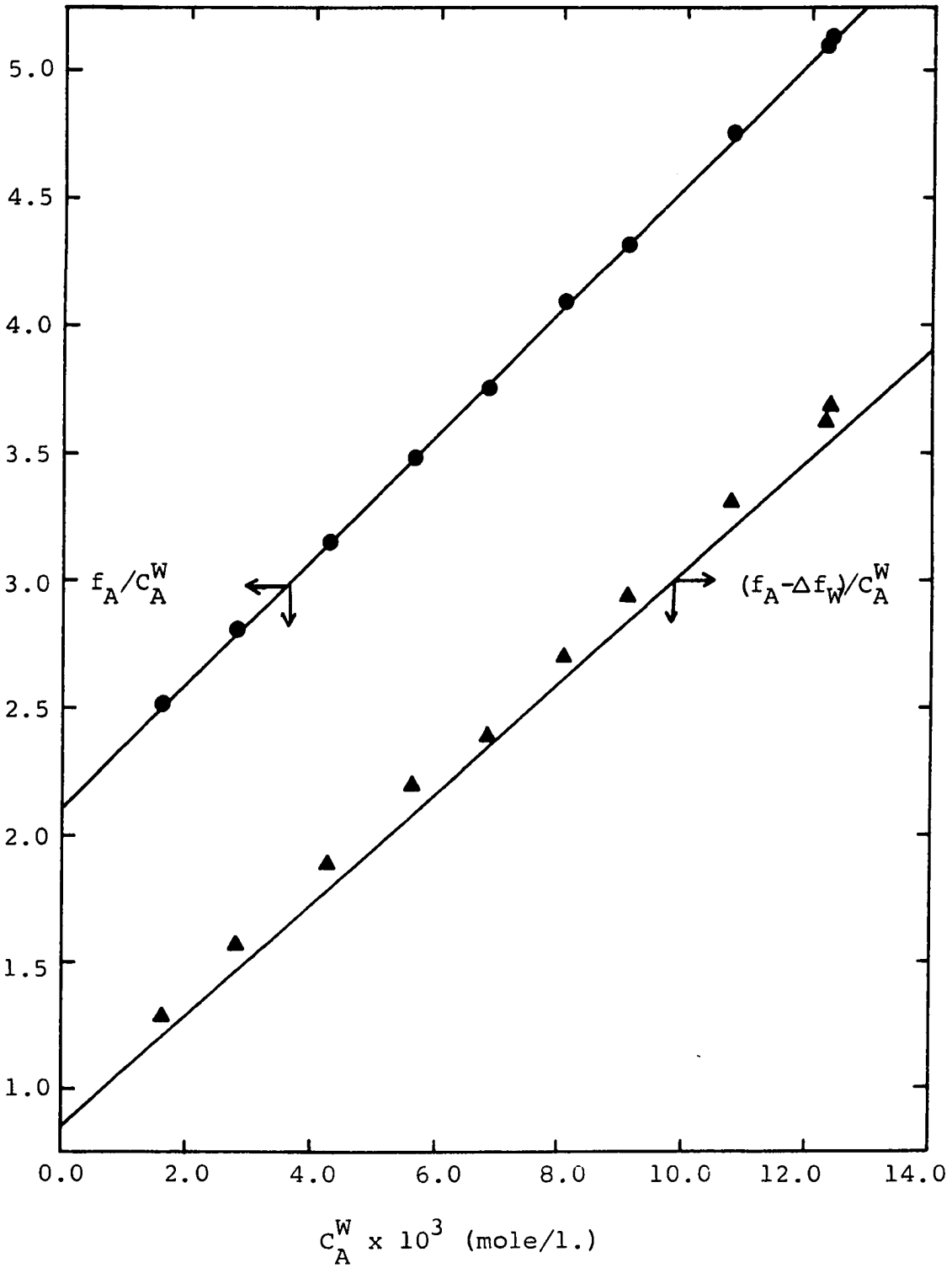


Figure IV. Distribution Plots for the Salicylic Acid-Water-Benzene System at 25°C.

Table V

Distribution Data for the Salicylic Acid-Water-Ethylene Dichloride System at 25°C

f_W(M)	f_A(M)	f_A^W(M)	C_A^W(M)	f_A/C_A^W	$(f_A - \Delta f_W)/C_A^W$
0.1374	0.0136	0.0037	0.0022	6.31	1.40
0.1480	0.0286	0.0062	0.0040	7.07	1.73
0.1533	0.0395	0.0077	0.0052	7.53	2.53
0.1610	0.0522	0.0092	0.0065	7.99	2.83
0.1680	0.0667	0.0109	0.0079	8.46	3.12
0.1762	0.0809	0.0123	0.0091	8.91	3.41
0.1829	0.0955	0.0137	0.0103	9.31	3.71
0.1905	0.1083	0.0148	0.0112	9.69	3.98
0.1956	0.1218	0.0158	0.0121	10.05	4.34
0.2016	0.1318	0.0167	0.0128	10.27	4.46

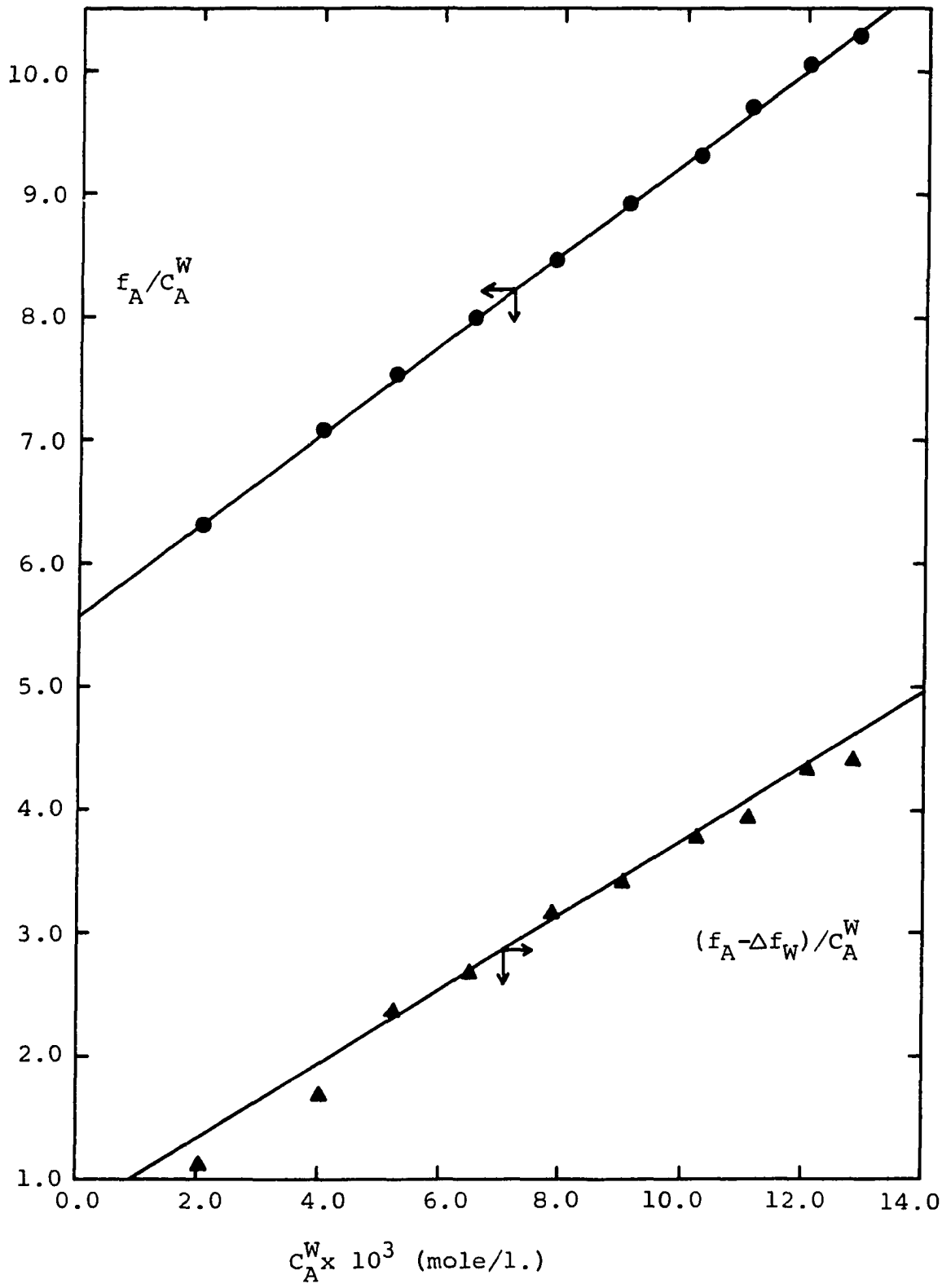


Figure V. Distribution Plots for the Salicylic Acid-Water-Ethylene Dichloride System at 25°C. Lines are calculated.

Table VI

Least Squares Slopes and

Intercepts of Distribution Plots

	f_A/C_A^W vs. C_A^W		$(f_A-\Delta f_W)/C_A^W$ vs. C_A^W	
System	Slope	Intercept	Slope	Intercept
Benzoic Acid-Water-Benzene	1095.0	1.696	1048.8	1.123
Salicylic Acid-Water-Carbon Tetrachloride	163.2	0.435	159.0	0.310
Salicylic Acid-Water-Benzene	242.9	2.118	220.0	0.929
Salicylic Acid-Water-Ethylene Dichloride	367.9	5.566	307.2	0.580

Table VII

Water Solubility Data for the

Benzoic Acid-Water-Benzene System at 25°C

a_W	f_A (M)	f_W (M)
0.400	0.0000	0.0129
	0.0683	0.0146
	0.1429	0.0160
	0.2109	0.0171
	0.2793	0.0181
	0.3343	0.0190
0.658	0.0000	0.0214
	0.0702	0.0253
	0.1457	0.0278
	0.2098	0.0304
	0.2833	0.0324
	0.3449	0.0339
0.790	0.0000	0.0264
	0.0699	0.0317
	0.1432	0.0354
	0.2048	0.0384
	0.2744	0.0405
	0.3451	0.0422

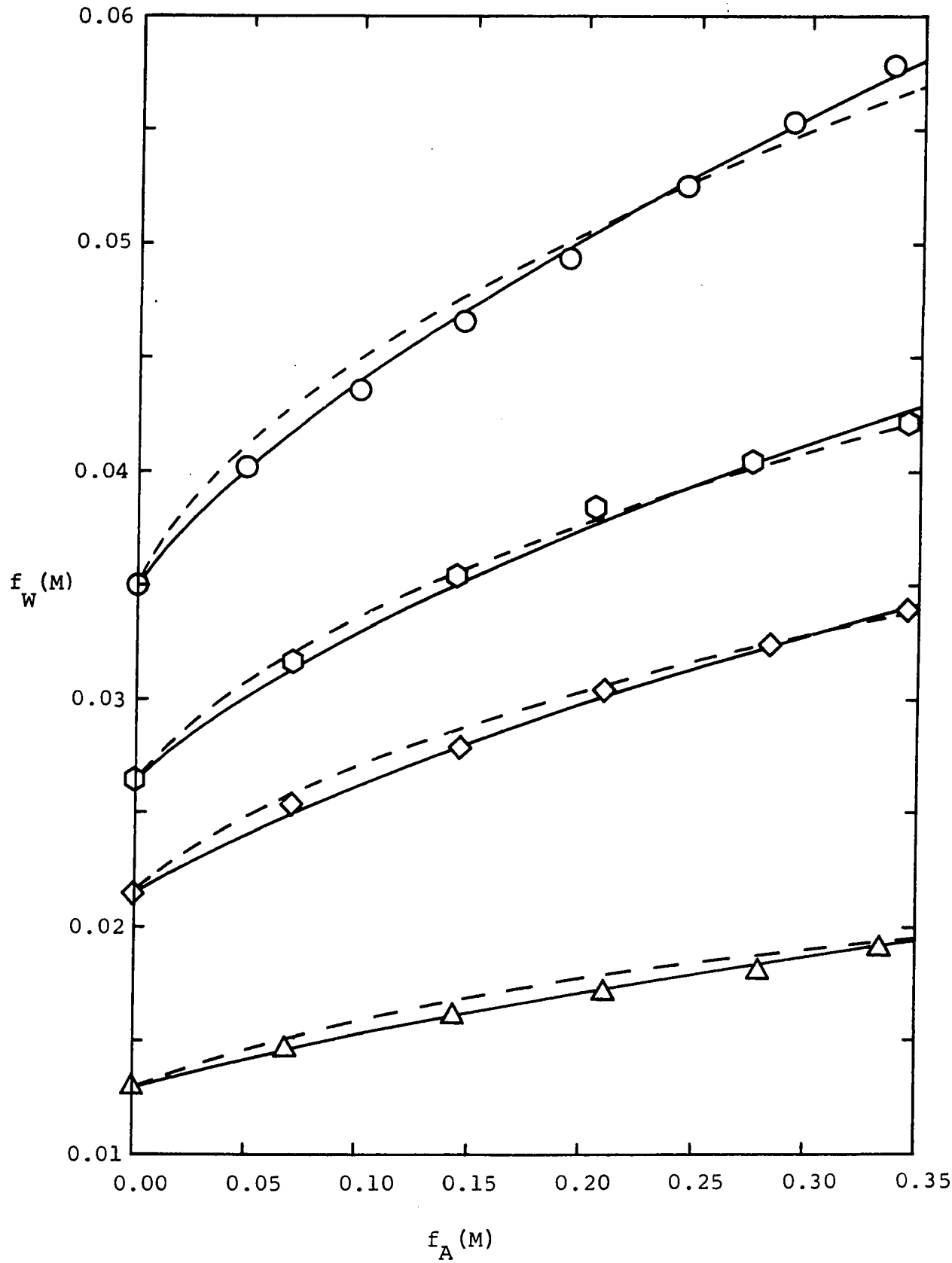


Figure VI. Water Solubility Plots for the Benzoic Acid-Water-Benzene System at 25°C. ○ , a_W = 1.0; ⬡ , a_W = 0.790; ◇ , a_W = 0.658; △ , a_W = 0.400. Lines are calculated; ------, Method A; ———, Method B.

Table VIII

Water Solubility Data for the

Salicylic Acid-Water-Carbon Tetrachloride System at 25°C

a_W	f_A (M)	f_W (M)
0.430	0.0000	0.0038
	0.0036	0.0039
	0.0062	0.0040
	0.0069	0.0040
	0.0166	0.0042
	0.0267	0.0042
	0.0276	0.0043
0.550	0.0000	0.0047
	0.0036	0.0051
	0.0062	0.0052
	0.0069	0.0054
	0.0166	0.0053
	0.0267	0.0057
	0.0276	0.0058
0.706	0.0000	0.0061
	0.0036	0.0064
	0.0062	0.0065
	0.0069	0.0066
	0.0166	0.0068
	0.0267	0.0072
	0.0276	0.0074

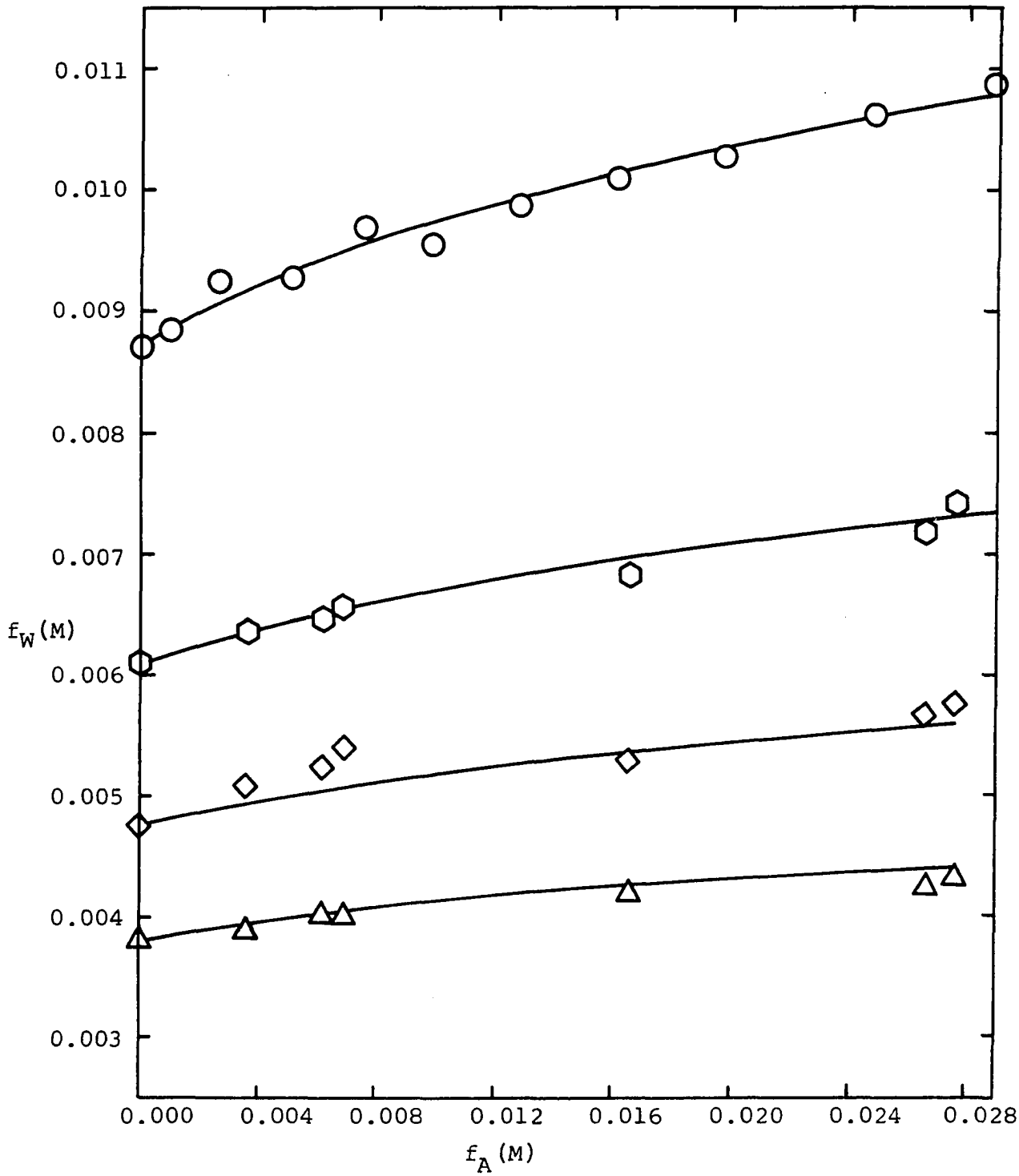


Figure VII. Water Solubility Plots for the Salicylic Acid-Water-Carbon Tetrachloride System at 25°C. ○ , a_W = 1.0; ⬡ , a_W ≐ 0.706; ◇ , a_W = 0.550; △ , a_W = 0.430. Lines are calculated.

Table IX

Water Solubility Data for the

Salicylic Acid-Water-Benzene System at 25°C

a_W	f_A (M)	f_W (M)
0.430	0.0000	0.0146
	0.0122	0.0172
	0.0251	0.0187
	0.0368	0.0193
	0.0497	0.0211
	0.0503	0.0209
0.550	0.0000	0.0194
	0.0122	0.0229
	0.0243	0.0246
	0.0366	0.0257
	0.0488	0.0273
	0.0525	0.0281
0.706	0.0000	0.0251
	0.0121	0.0292
	0.0243	0.0317
	0.0367	0.0338
	0.0491	0.0358
	0.0554	0.0369

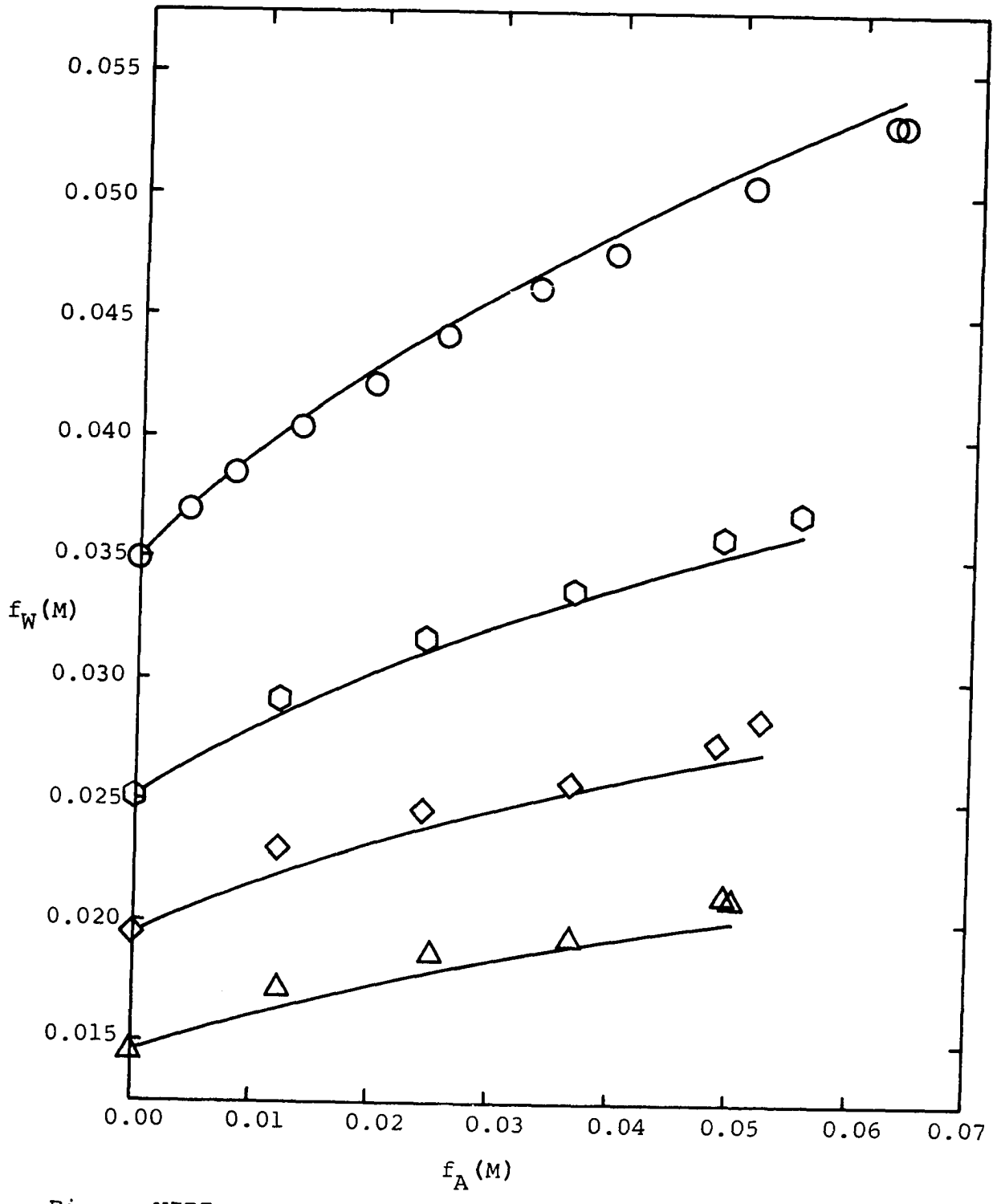


Figure VIII. Water Solubility Plots for the Salicylic Acid-Water-Benzene System at 25°C. ○, a_W = 1.0; ⬡, a_W = 0.706; ◇, a_W = 0.550; △, a_W = 0.430. Lines are calculated.

Table X

Water Solubility Data for the

Salicylic Acid-Water-Ethylene Dichloride System at 25°C

a_W	f_A(M)	f_W(M)
0.468	0.0000	0.0541
	0.0255	0.0609
	0.0550	0.0667
	0.0811	0.0711
	0.0951	0.0729
	0.0958	0.0738
0.670	0.0000	0.0790
	0.0265	0.0906
	0.0552	0.0996
	0.0792	0.1068
	0.1073	0.1141
	0.1078	0.1153
0.880	0.0000	0.1084
	0.0269	0.1219
	0.0523	0.1369
	0.0828	0.1456
	0.1099	0.1575
	0.1233	0.1646

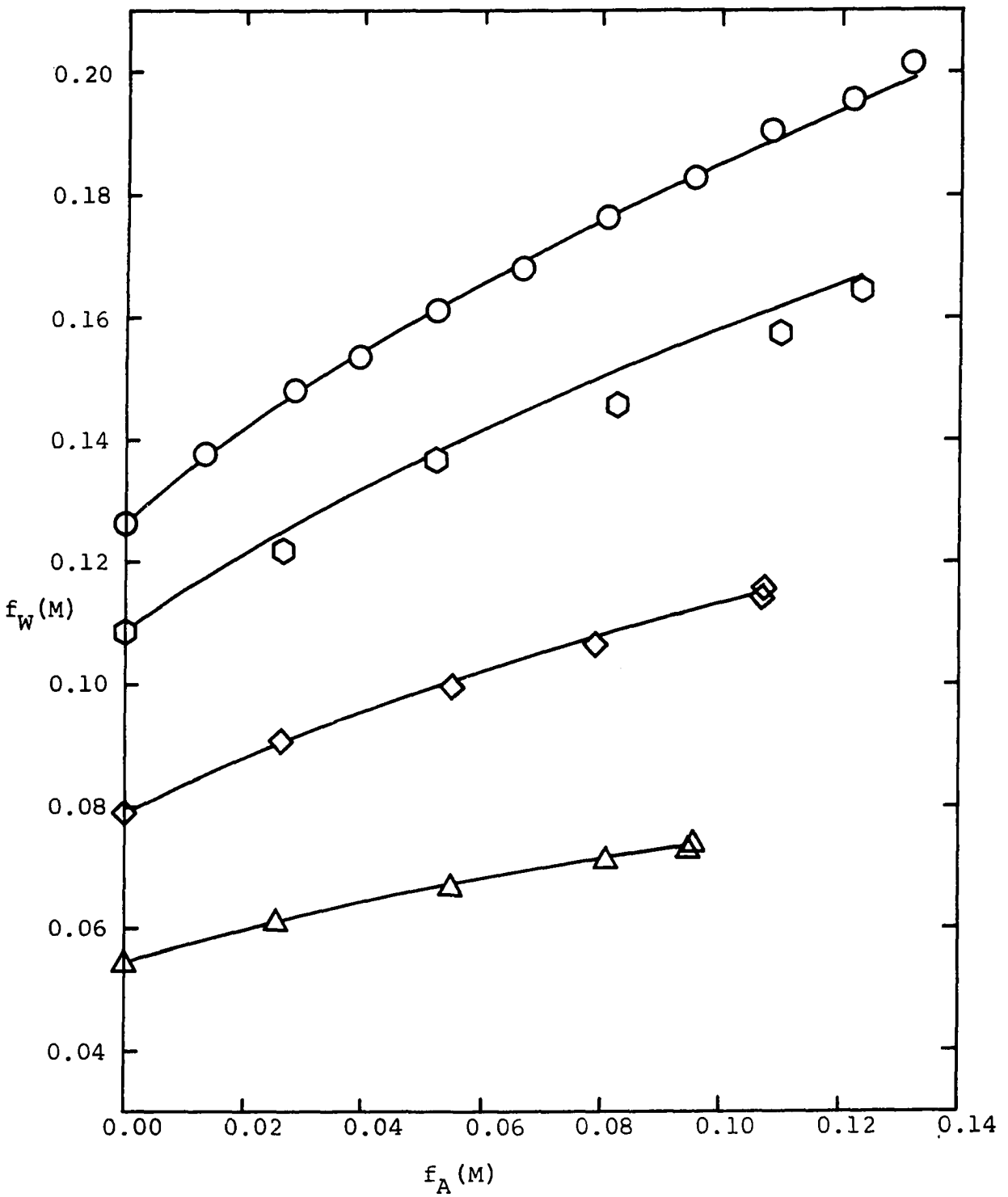


Figure IX. Water Solubility Plots for the Salicylic Acid-Water-Ethylene Dichloride System at 25°C. ○, a_W = 1.0; ⬡, a_W = 0.880; ◇, a_W = 0.670; △, a_W = 0.468. Lines are calculated.

Table XI

Water and Acid Solubility Data for the

Salicylic Acid-Water-Benzene System at 25°C

a_W	f_W(M)	f_A(M)
0.000	0.0000	0.0445
0.400	0.0186	0.0500
0.426	0.0190	0.0503
0.430	0.0209	0.0503
0.498	0.0236	0.0514
0.528	0.0247	0.0520
0.550	0.0284	0.0525
0.658	0.0323	0.0544
0.706	0.0369	0.0554
0.708	0.0333	0.0550
0.776	0.0387	0.0567
0.832	0.0430	0.0580
0.934	0.0493	0.0602
1.000	0.0531	0.0614

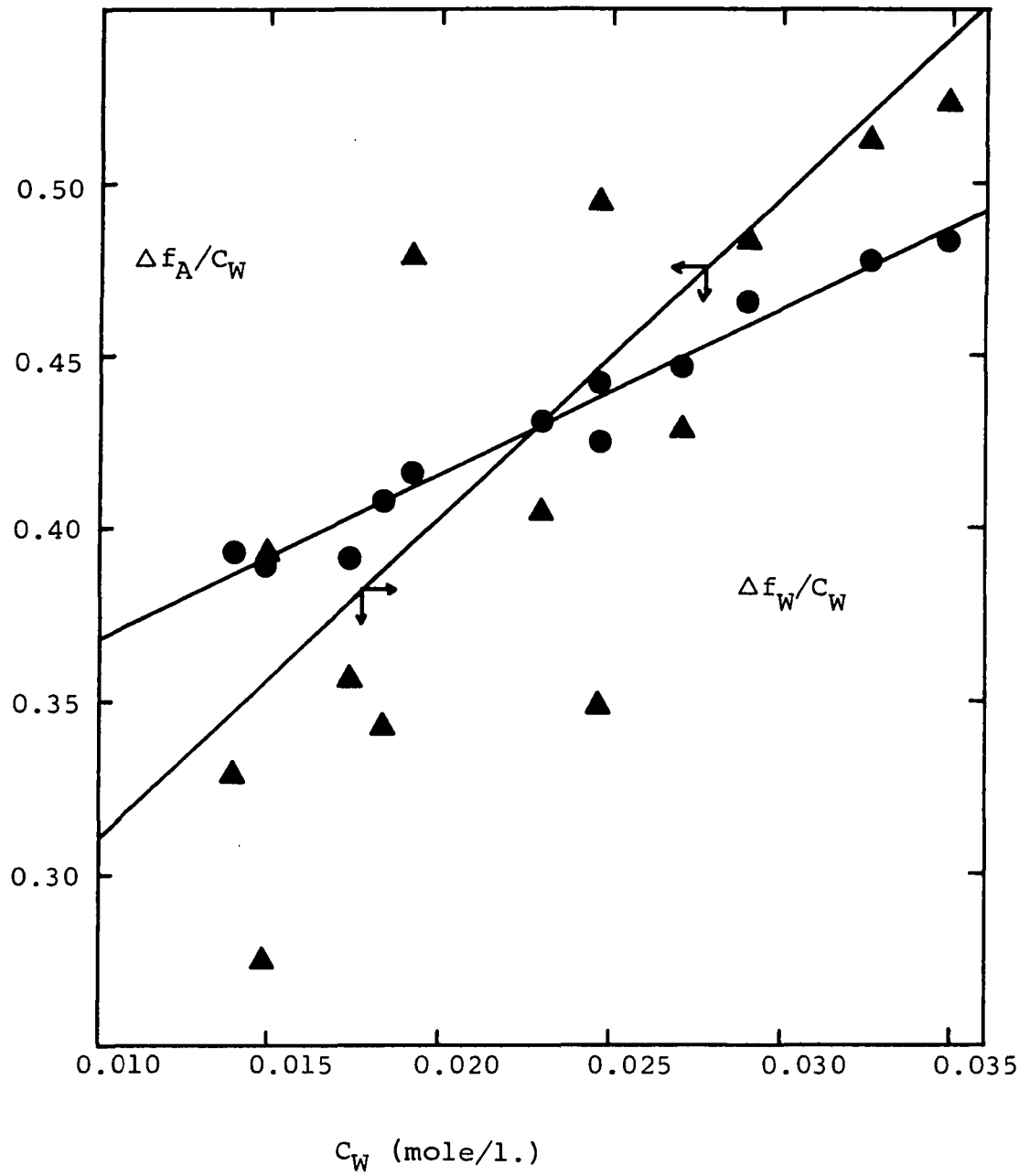


Figure X. Water and Acid Solubility Plots for the Salicylic Acid-Water-Benzene System at 25°C. ●, $\Delta f_A/C_W$; ▲, $\Delta f_W/C_W$. Lines are calculated.

Table XII

Water and Acid Solubility Data for the

Salicylic Acid-Water-Ethylene Dichloride System at 25°C

a_W	f_W(M)	f_A(M)
0.000	0.0000	0.0765
0.156	0.0226	0.0816
0.250	0.0366	0.0851
0.400	0.0621	0.0922
0.468	0.0738	0.0958
0.498	0.0805	0.0972
0.658	0.1125	0.1068
0.670	0.1153	0.1078
0.776	0.1368	0.1146
0.832	0.1529	0.1190
0.880	0.1646	0.1233
0.934	0.1797	0.1278
1.000	0.2000	0.1333

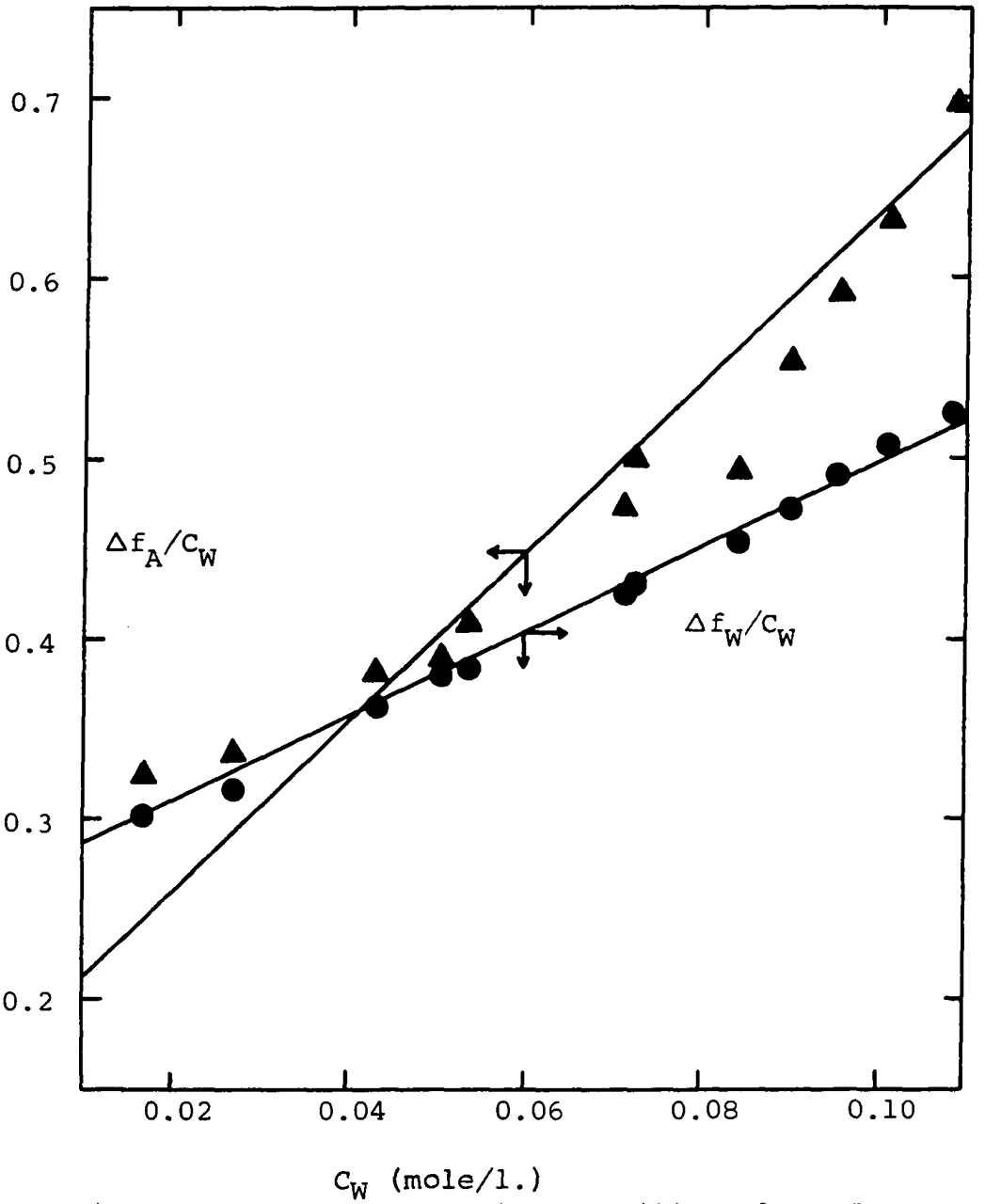


Figure XI. Water and Acid Solubility Plots for the Salicylic Acid-Water-Ethylene Dichloride System at 25°C. ●, $\Delta f_A/C_W$; ▲, $\Delta f_W/C_W$. Lines are calculated.

Table XIII

Results of the Nonlinear Least Squares Treatment for the Benzoic Acid-Water-Benzene System at 25°C

	Method A	Method B
K_{20}(l./mole)	589[a]	298±25
K_{11}(l./mole)	12.4±1.5	0.7±2.0
K_{12}($l.^2$/mole^2)	248±30	222±18
K_{21}($l.^2$/mole^2)	582±81	602±32
K_D	0.950±0.002	1.31±0.05
S_R	0.0357	0.0298
S_W(mole/l.)	0.00071	0.00043

(a) Obtained by extrapolating the results of Allen, Watkinson and Webb (51) to 25°C.

Table XIV

Results of the Nonlinear Least Squares Treatment for the Salicylic Acid Systems at 25°C

	Carbon Tetrachloride	Benzene	Ethylene Dichloride
K_{20}(l./mole)	630±80	55.5±5.6	14.1±2.2
K_{11}(l./mole)	11.0±6.0	7.20±2.55	1.63±0.87
K_{12}(l^2/mole^2)	1840±305	288±20	63.6±4.5
K_{21}(l^2/mole^2)	3280±1100	403±20	72.1±5.0
K_D	0.352±0.020	1.32±0.05	2.90±0.20
S_R	0.0173	0.0133	0.0301
S_W(mole/l.)	0.00012	0.00109	0.00480
S_A(mole/l.)	–	0.000142	0.000301

Table XV

Vapor Pressure Lowering Data for the Benzoic Acid-Benzene System at 25°C

f_A (M)	P_1^o (mm Hg)	ΔP (mm Hg)	f_A' (M)
0.0129	95.051	0.062	0.0073
0.0165	95.050	0.079	0.0093
0.0200	95.046	0.087	0.0102
0.0239	95.045	0.106	0.0125
0.0273	95.048	0.121	0.0142
0.0306	95.052	0.139	0.0163
0.0341	95.044	0.150	0.0176
0.0375	95.048	0.165	0.0194
0.0413	95.049	0.181	0.0213
0.0436	95.051	0.191	0.0225

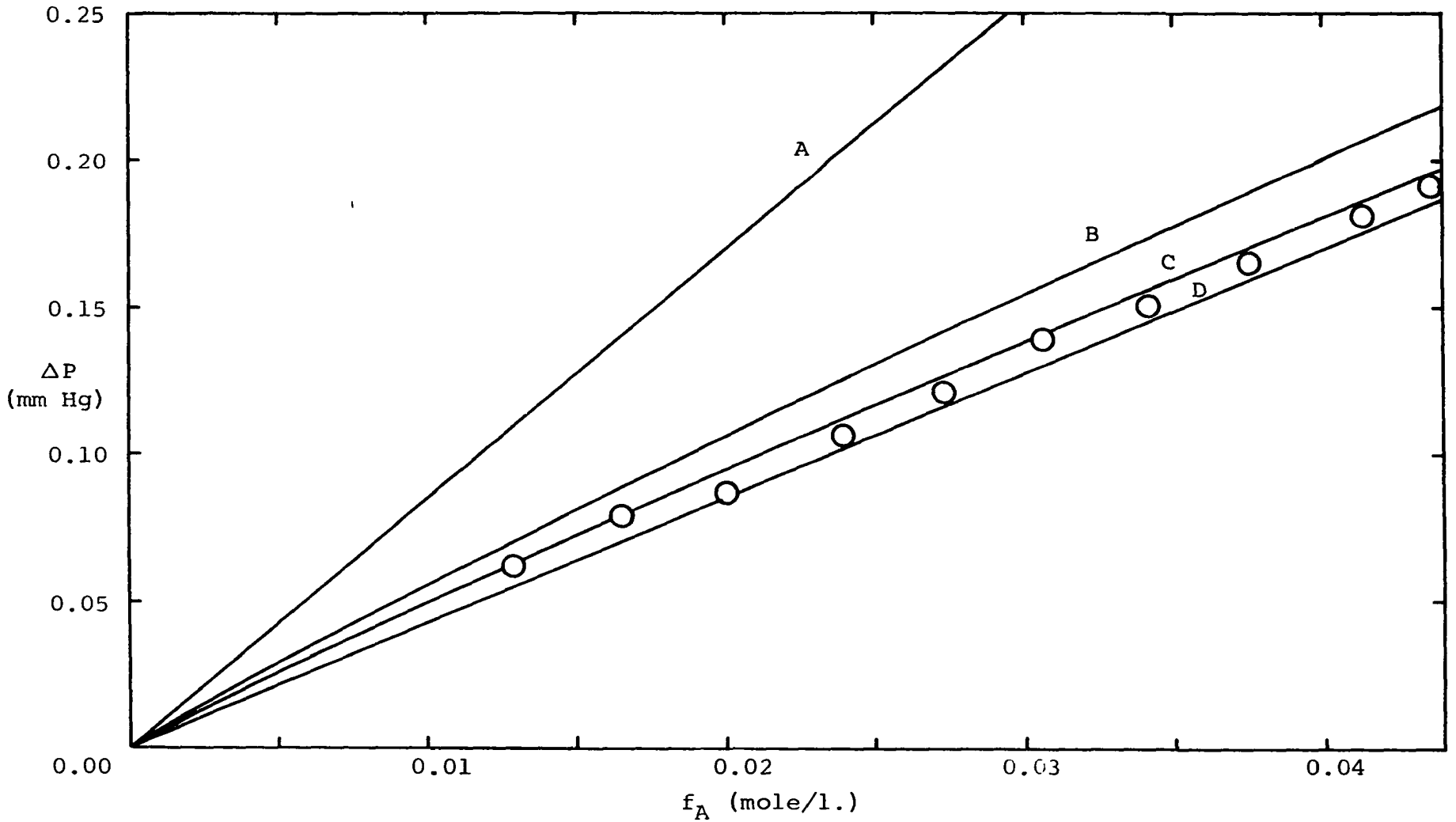


Figure XII. Vapor Pressure Lowering Plot for the Benzoic Acid-Benzene System at 25°C. Lines are calculated. A, monomer line; B, K_{20} = 300 l./mole; C, K_{20} = 2,000 l./mole; D, dimer line.

Table XVI

Vapor Pressure Lowering Data for the

Salicylic Acid-Carbon Tetrachloride System at 25°C

f_A (M)	P_1^o (mm Hg)	ΔP (mm Hg)	f_A' (M)
0.0091	113.886	0.052	0.0047
0.0109	113.891	0.061	0.0055
0.0129	113.885	0.067	0.0061
0.0150	113.885	0.085	0.0077
0.0168	113.901	0.099	0.0089
0.0191	113.890	0.105	0.0095
0.0208	113.884	0.109	0.0098
0.0225	113.883	0.124	0.0112
0.0241	113.878	0.133	0.0120
0.0259	113.898	0.151	0.0136
0.0276	113.883	0.158	0.0143

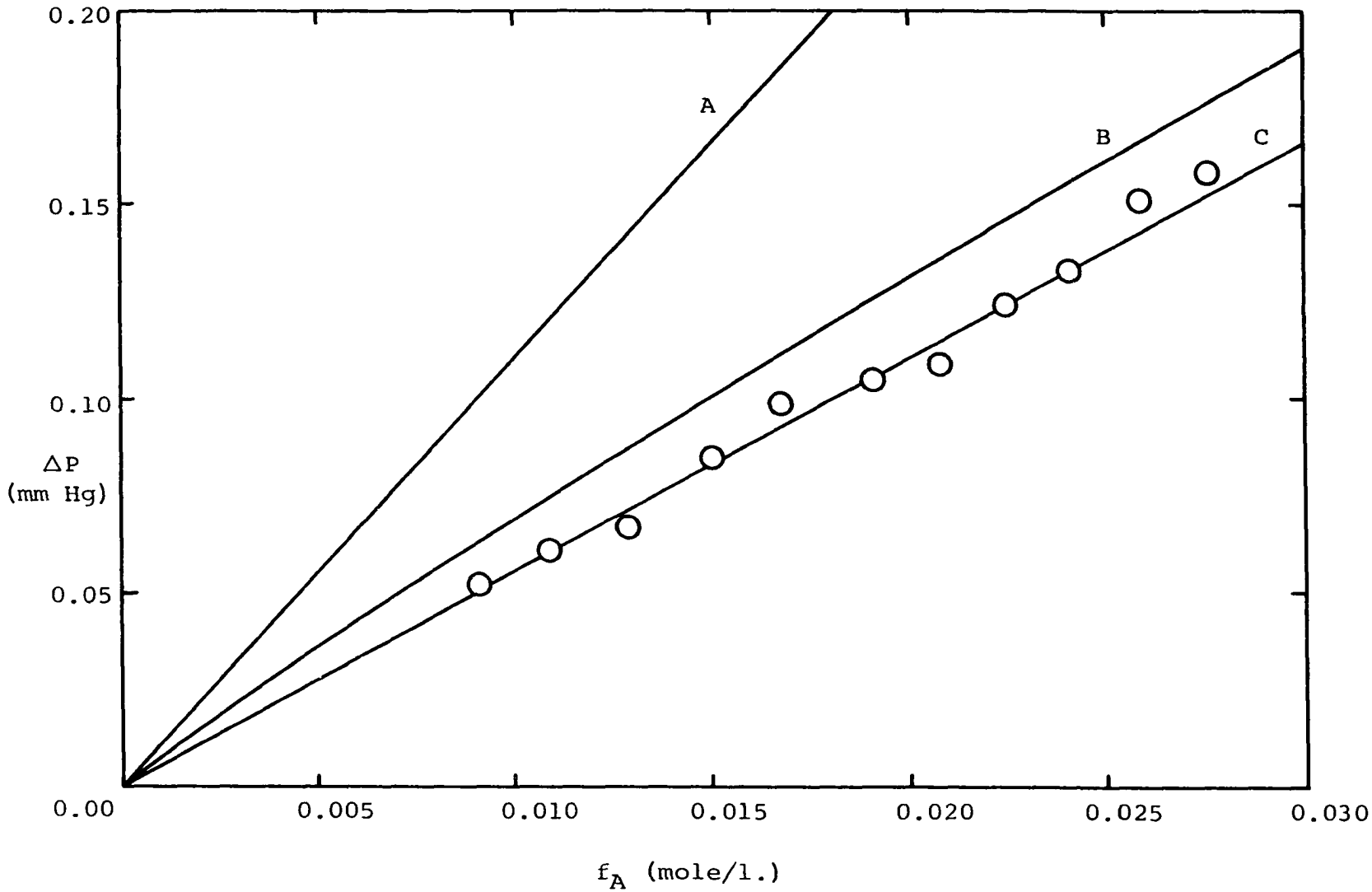


Figure XIII. Vapor Pressure Lowering Plot for the Salicylic Acid-Carbon Tetrachloride System at 25°C. Lines are calculated. A, monomer line; B, K_{20} = 630 l./mole; C, dimer line.

Table XVII

Vapor Pressure Lowering Data for the

Salicylic Acid-Benzene System at 25°C

f_A(M)	P_1^o(mm Hg)	ΔP(mm Hg)	f_A'(M)
0.0134	95.031	0.082	0.0096
0.0164	95.031	0.098	0.0115
0.0198	95.032	0.108	0.0127
0.0226	95.060	0.125	0.0147
0.0264	95.048	0.138	0.0162
0.0294	95.055	0.157	0.0185
0.0331	95.057	0.174	0.0205
0.0369	95.060	0.196	0.0230
0.0415	95.053	0.217	0.0255
0.0450	95.062	0.234	0.0275

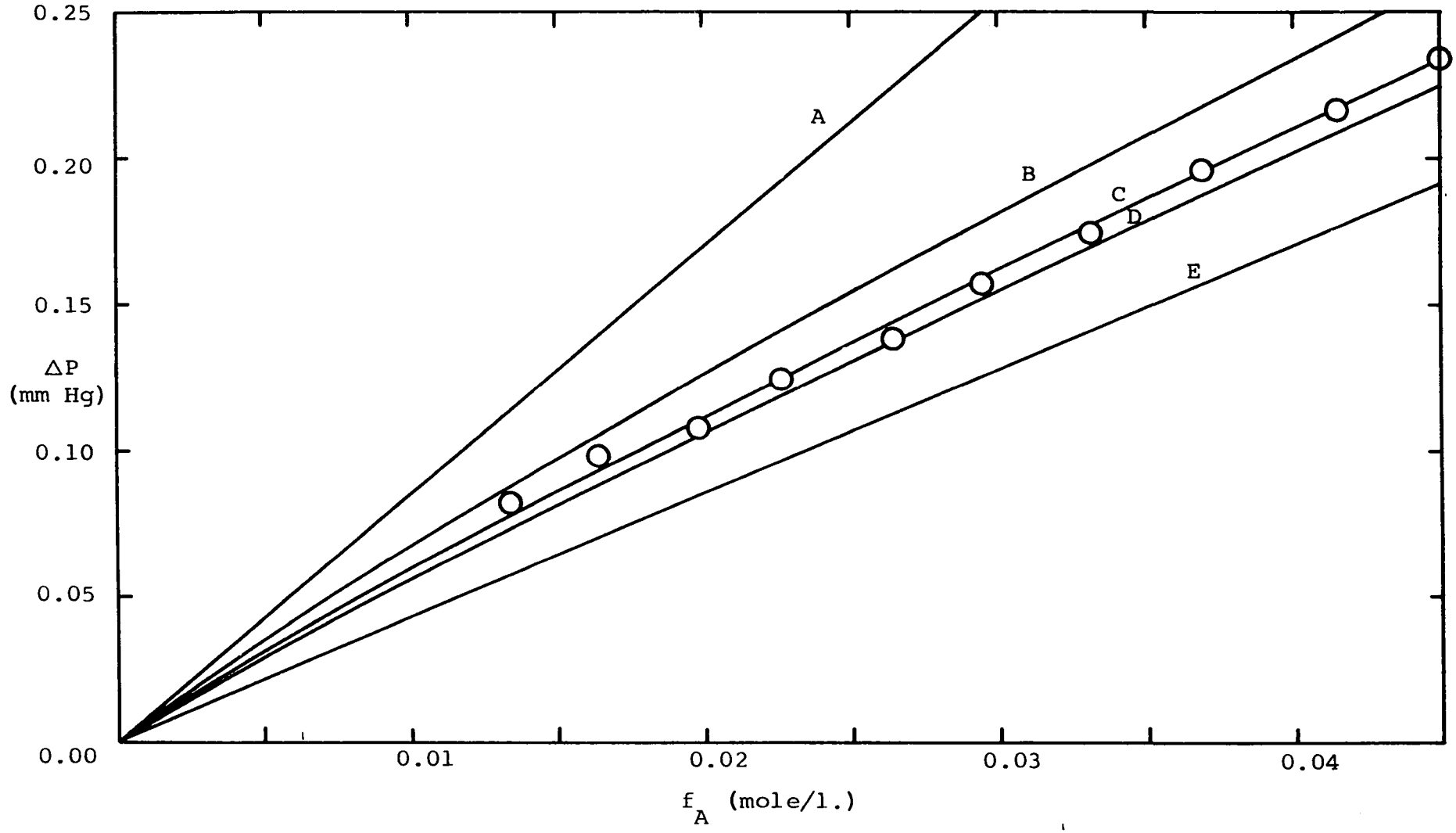


Figure XIV. Vapor Pressure Lowering Plot for the Salicylic Acid-Benzene System at 25°C. Lines are calculated. A, monomer line; B, K_{20} = 55 l./mole; C, K_{20} = 180 l./mole; D, K_{20} = 300 l./mole; E, dimer line.

Table XVIII

Vapor Pressure Lowering Data for the

Salicylic Acid-Ethylene Dichloride System at 25°C

f_A (M)	P_1^o (mm Hg)	ΔP (mm Hg)	f_A' (M)
0.0256	78.766	0.113	0.0181
0.0315	78.755	0.146	0.0233
0.0366	78.751	0.167	0.0267
0.0415	78.738	0.186	0.0297
0.0472	78.734	0.205	0.0328
0.0518	78.735	0.217	0.0347
0.0577	78.733	0.244	0.0390
0.0617	78.726	0.253	0.0404
0.0680	78.739	0.284	0.0454
0.0735	78.731	0.299	0.0478
0.0795	78.731	0.331	0.0529

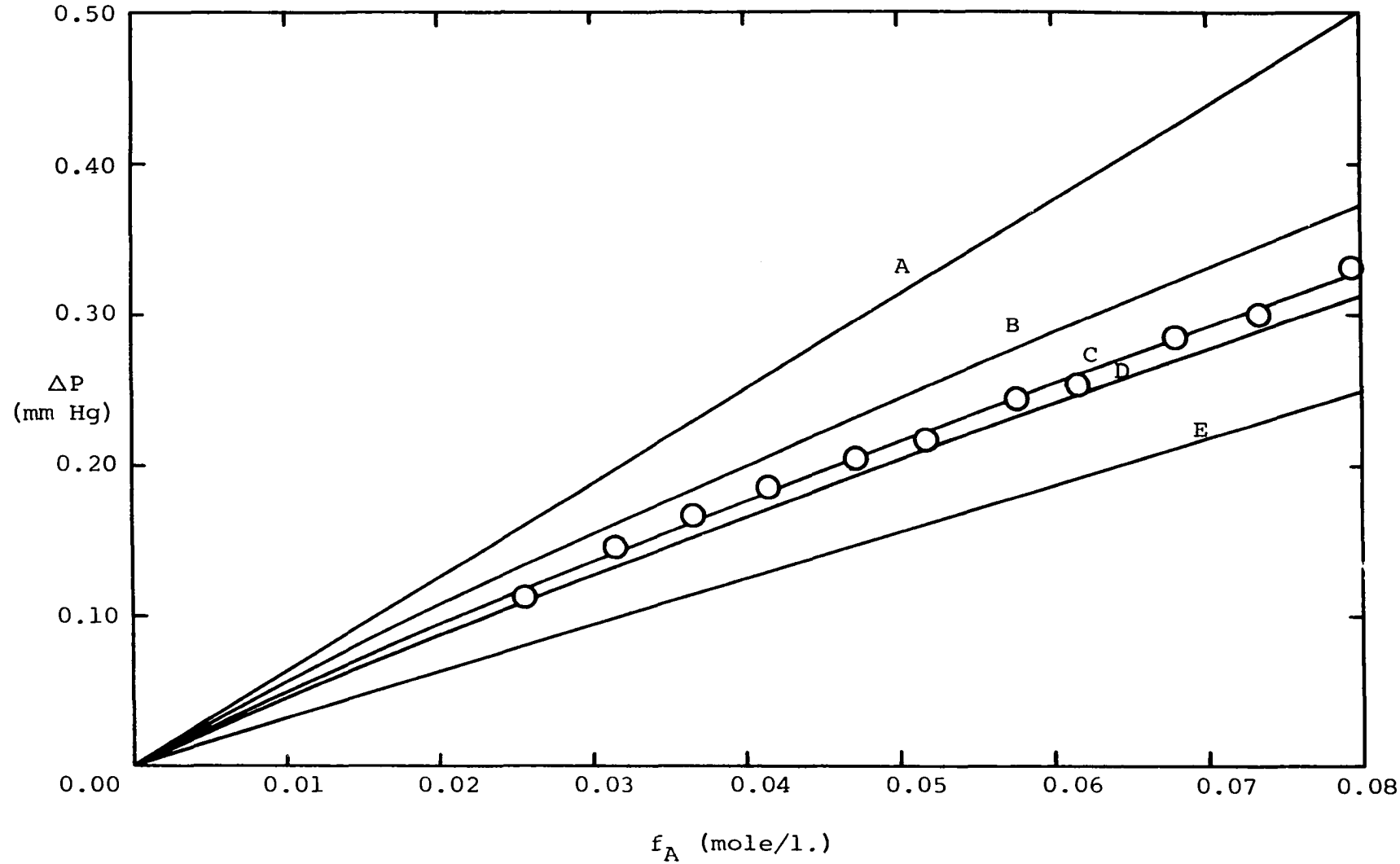


Figure XV. Vapor Pressure Lowering Plot for the Salicylic Acid-Ethylene Dichloride System at 25°C. Lines are calculated. A, monomer line; B, K_{20} = 14 l./mole; C, K_{20} = 45 l./mole; D, K_{20} = 75 l./mole; E, dimer line.

CHAPTER IV

DISCUSSION AND CONCLUSIONS

Distribution and Solubility Results

The root-mean-square deviations given in Table XIII and the calculated lines in Figures II and VI demonstrate the success achieved in fitting the distribution and water solubility data for the benzoic acid-benzene system. By comparing the data fits obtained by the two methods, it can be seen that a somewhat better fit is obtained by method B. The slightly higher root-mean-square deviations obtained by method A are not surprising since fixing the value of the dimerization constant reduces the number of parameters which are adjusted to fit the data. Both method A and method B lead to a reasonable fit of all the data, consistent with the uncertainties in the distribution and water solubility measurements.

Somewhat different results have been obtained by the two data-fitting methods. The value of monomer monohydrate association constant, K_{11}, is 0.7 ± 2.0 l./mole according to

method B and 12.4±1.5 l./mole according to method A. The former value is small and has a large relative error, implying that the monomer monohydrate is not an important species. The latter value indicates that the monomer monohydrate is present in significant concentrations. Values of association constants for the monomer dihydrate, K_{12}, and the dimer monohydrate, K_{21}, agree to within their standard errors as determined by both method A and method B.

The relative importance of various hydrated and associated benzoic acid species can be visualized more easily by directly comparing species concentrations over a range of total acid concentration. For distribution systems in which the nonaqueous phase is saturated with water, the total acid concentration is expressed by

$$f_A = C_A + K_{11}C_W^{o}C_A + K_{12}C_W^{o2}C_A + 2K_{20}C_A^2 + 2K_{21}C_W^{o}C_A^2 \quad . \tag{44}$$

Using equilibrium constants determined by the least squares data analyses and the appropriate value of the constant, C_W^o, individual species concentrations and the total acid concentration can be calculated for various values of the acid monomer concentration, C_A. Table XIX contains values of

Table XIX

Calculated Molar Concentrations of Acid Species for the Benzoic Acid-Water-Benzene System

Method A

$C_W^o = 0.0349$

$f_A = C_A + (12.4)(0.0349)C_A + (248)(0.0349)^2 C_A + (2)(589)C_A^2 + (2)(582)(0.0349)C_A^2$

$f_A = C_A + (0.433)C_A + (0.302)C_A + (2)(589)C_A^2 + (2)(20.3)C_A^2$

C_A	C_{AW}	C_{AW_2}	C_{A_2}	C_{AW_2}	f_A	% of acid hydrated
0.0070	0.0030	0.0021	0.0289	0.0010	0.0719	9.9
0.0090	0.0039	0.0027	0.0477	0.0016	0.1142	8.6
0.0110	0.0048	0.0033	0.0713	0.0025	0.1667	7.9
0.0130	0.0056	0.0039	0.0995	0.0034	0.2283	7.1
0.0150	0.0065	0.0045	0.1325	0.0046	0.3002	6.7

Table XIX (continued)

Method B

$C_W^o = 0.0349$

$f_A = C_A + (0.7)(0.0349)C_A + (222)(0.0349)^2 C_A + (2)(298)C_A^2 + (2)(602)(0.0349)C_A^2$

$f_A = C_A + (0.0244)C_A + (0.270)C_A + (2)(298)C_A^2 + (2)(21.0)C_A^2$

C_A	C_{AW}	C_{AW_2}	C_{A_2}	C_{A_2W}	f_A	% of acid hydrated
0.0090	0.0002	0.0024	0.0241	0.0017	0.0632	9.5
0.0120	0.0003	0.0032	0.0429	0.0030	0.1073	8.8
0.0150	0.0004	0.0041	0.0671	0.0047	0.1631	8.5
0.0180	0.0004	0.0049	0.0966	0.0068	0.2301	8.2
0.0210	0.0005	0.0057	0.1314	0.0092	0.3084	8.0

species concentrations calculated from equilibrium constants obtained by both method A and method B. Values of C_A have been chosen so that the resulting values of f_A approximately coincide with the concentration range covered in the actual distribution experiment.

Examination of the calculated species concentrations in the table reveals that the major species in the system is the anhydrous acid dimer. However, the predicted concentrations of hydrated species are significant as indicated by the values given in the last column which represent the percent of the acid which is hydrated. As expected from the values of the association constants, the monomer monohydrate concentrations are much lower for method B than for method A. For a given value of f_A, calculated concentrations of the other species are nearly the same for both methods.

A question naturally arises concerning which method, A or B, is more satisfactory for correlating self-association and hydration data for the benzoic acid-benzene system. It is felt that method A, which assumes the dimerization constant to be 589 l./mole, is the better method for fitting the data. As illustrated by Allen, Watkinson, and Webb (51), this value obtained by infrared spectroscopy is in good agreement with values obtained by other methods. The

ebullioscopic results of Allen and Caldin (30), the isopiestic results of Wall and Banes (32), and the cryoscopic results of Barton and Kraus (28) and Izmailov and Partskhaladze (82) all conform excellently to a plot of log K_{20} versus 1/T (10,51). Since all of these investigations have dealt with presumably dry solutions, the value, 589 l./mole, for the dimerization constant of benzoic acid in benzene at 25°C is probably a more reliable value than 298 l./mole obtained by method B. An additional attractive feature of method A is the fewer number of unknown constants to be evaluated from the distribution and water solubility data. Independent knowledge concerning the extent of self-association of the acid is therefore useful in allowing hydration of the acid to be studied more effectively.

Unfortunately, the self-association of salicylic acid in dry solvents has received little attention. Unlike the case of the benzoic acid-benzene system, it is not possible to infer the extent of acid dimerization in the salicylic acid systems from the results of previous studies. Therefore, the method which has been used in fitting the distribution and solubility data for the salicylic acid systems involves the determination of all five equilibrium constants from the data as in method B which has been discussed. Close

fits of the data have been obtained for each of the systems as demonstrated by the root-mean-square deviations given in Table XIV and the calculated lines in Figures III, IV and V (distribution data), in Figures VII, VIII and IX (water solubility data), and in Figures X and XI (water and acid solubility data).

The water and acid solubility data contained in Tables XI and XII and plotted in Figures X and XI deserve special discussion. This type of data has been obtained only for the salicylic acid-benzene and salicylic acid-ethylene dichloride systems for the reasons discussed in Chapter III. The additional solubility data are valuable since they provide further experimental evidence from which to determine equilibrium constants. Moreover, by plotting the acid solubility data as $\Delta f_A/C_W$ versus C_W and the water solubility data as $\Delta f_W/C_W$ versus C_W, it is possible to learn a great deal about the nature of hydrated species present in the system. This becomes apparent by considering equations 35 and 36 which were developed in the previous chapter and comparing the data plots given in Figures X and XI. Assuming that the set of hydrated species which are proposed to exist in the systems is the correct one, the solubility plots for each system should be linear with positive slopes and

positive intercepts. Furthermore, the intercept of the $\Delta f_A/C_W$ plot should be greater than the intercept of the $\Delta f_W/C_W$ plot, and the slope of the former should be exactly one-half the slope of the latter. The acid solubility data conform very well to these predictions and to the calculated lines as shown in the figures. Unfortunately, the plots are very sensitive to error in the experimental measurements, particularly in the case of the $\Delta f_W/C_W$ points, which are based on the less precise water solubility data. In spite of the scatter, the water solubility data also appear to verify the hydration predictions, and agreement with the calculated line is within possible experimental errors in the water determinations.

It is interesting to compare the magnitudes of the equilibrium constants given in Table XIV for the three salicylic acid systems. The value of each association constant decreases in going from carbon tetrachloride, to benzene, to ethylene dichloride, whereas the value of the distribution constant increases with solvent in the same order. The observed behavior is precisely what should be expected since solvent reactivity increases in the order: carbon tetrachloride<benzene<ethylene dichloride. The effect of solvent on the dimerization process is considered in more detail later

in this chapter.

It is also interesting to compare association constants obtained for the salicylic acid-benzene system with the corresponding constants for the benzoic acid-benzene system. The greatest difference occurs in the dimerization constants for the two acids; the value of K_{20} for salicylic acid (55.5 l./mole) being much smaller than the value for benzoic acid (589 l./mole). The main cause of this behavior is presumably the occurrence of intramolecular hydrogen bonding involving the hydroxyl group of salicylic acid, which decreases the effectiveness of the carboxyl group toward intermolecular association (83). Evidence of the intramolecular hydrogen bond in salicylic acid is also provided by some of its other properties. For example, Branch and Yabroff (84) have pointed out that salicylic acid is a much stronger acid than benzoic, m-hydroxybenzoic, and p-hydroxybenzoic acids because of the effect of the hydrogen bond with the hydroxyl group in partially saturating the proton affinity of the acid anion. Maryott, Hobbs, and Gross (85) have proposed that a correlation exists between the dimerization constants of certain carboxylic acids in benzene and their ionization constants in water; i.e., the stronger the acid in water the less is its tendency to associate in benzene. Certainly this

is true in the present case, since intramolecular hydrogen bonding apparently causes salicylic acid to be more ionized in water and also less associated in benzene than benzoic acid. However, Allen and Caldin (10) have compared ionization constants with dimerization constants determined from dielectric measurements for a large number of carboxylic acids and they conclude that the parallelism which exists is only approximate.

The hydration constants of salicylic acid and benzoic acid in benzene differ much less than the values of K_{20}. Assuming that hydration of the acids occurs through hydrogen bonding of water molecules to the carboxyl group, intramolecular hydrogen bonding in salicylic acid should decrease its hydration compared to benzoic acid. The effect of intramolecular hydrogen bonding in decreasing hydration should be less than its effect in decreasing dimerization, since both acid monomers which react to form a dimer are likely deactivated to some extent by the hydroxyl group. Therefore, decreases in the hydration constants are expected to be small compared to the observed decrease in K_{20}. This is seen to be the case for K_{11} if the value 12.4 l./mole is taken for benzoic acid compared to 7.20 l./mole for salicylic acid. The values of K_{21} also conform to this prediction, decreasing

from 582 $l.^2/mole^2$ for benzoic acid to 403 $l.^2/mole^2$ for salicylic acid. However, K_{12} is slightly smaller for benzoic acid (248 $l.^2/mole^2$) than for salicylic acid (288 $l.^2/mole^2$). This behavior cannot be explained so readily in terms of intramolecular hydrogen bonding. A possible explanation is that the salicylic acid molecule has more sites available for attaching water than does the benzoic acid molecule.

Table XX contains concentrations of salicylic acid species calculated for each solvent system from equation 44 and the least squares equilibrium constants given in Table XIV. As for the benzoic acid-benzene system, the anhydrous acid dimer is in each case the most highly concentrated species, but hydrated acid species again contribute significantly to the total acid concentration, f_A. The hydration percentages increase considerably in going from carbon tetrachloride, to benzene, to ethylene dichloride; this appears to be a result of the increased importance of mass action as solvent reactivity (and hence, water solubility) increases. It is apparent that salicylic acid is hydrated to a greater extent in benzene than is benzoic acid. The major difference is that much more benzoic acid exists as the anhydrous dimer at a given total acid concentration, as noted earlier.

The results which have been obtained from the distri-

Table XX

Calculated Molar Concentrations for the

Salicylic Acid Systems at 25°C

Carbon Tetrachloride

$C_W^o = 0.0087$

$f_A = C_A + (11.0)(0.0087)C_A + (1840)(0.0087)^2 C_A + (2)(3280)(0.0087)C_A^2 + (2)(630)C_A^2$

$f_A = C_A + (0.096)C_A + (0.139)C_A + (2)(630)C_A^2 + (2)(28.5)C_A^2$

C_A	C_{AW}	C_{AW_2}	C_{A_2}	C_{A_2W}	f_A	% of acid hydrated
0.0010	0.0001	0.0001	0.0006	------	0.0024	8.3
0.0020	0.0002	0.0003	0.0025	0.0001	0.0077	9.1
0.0030	0.0003	0.0004	0.0057	0.0003	0.0157	8.2
0.0040	0.0004	0.0006	0.0101	0.0005	0.0262	7.6
0.0050	0.0005	0.0007	0.0157	0.0007	0.0390	6.6

Table XX (continued)

Benzene

$C_W^o = 0.0349$

$f_A = C_A + (7.20)(0.0349)C_A + (288)(0.0349)^2 C_A + (2)(55.5)C_A^2 + (2)(403)(0.0349)C_A^2$

$f_A = C_A + (0.251)C_A + (0.351)C_A + (2)(55.5)C_A^2 + (2)(14.1)C_A^2$

C_A	C_{AW}	C_{AW_2}	C_{A_2}	C_{A_2W}	f_A	% of acid hydrated
0.0040	0.0010	0.0014	0.0009	0.0002	0.0086	32.5
0.0070	0.0018	0.0025	0.0027	0.0007	0.0181	31.5
0.0100	0.0025	0.0035	0.0056	0.0014	0.0300	29.3
0.0130	0.0033	0.0046	0.0094	0.0024	0.0455	27.9
0.0160	0.0040	0.0056	0.0142	0.0036	0.0612	27.4

Table XX (continued)

Ethylene Dichloride

$C_W^o = 0.1083$

$f_A = C_A + (1.63)(0.1083)C_A + (63.6)(0.1083)^2 C_A + (2)(14.1)C_A^2 + (2)(72.1)(0.1083)C_A^2$

$f_A = C_A + (0.176)C_A + (0.746)C_A + (2)(14.1)C_A^2 + (2)(7.81)C_A^2$

C_A	C_{AW}	C_{AW_2}	C_{A_2}	C_{A_2W}	f_A	% of acid hydrated
0.0040	0.0007	0.0028	0.0002	0.0001	0.0081	45.7
0.0120	0.0021	0.0089	0.0020	0.0011	0.0292	45.2
0.0200	0.0035	0.0149	0.0056	0.0031	0.0558	44.1
0.0280	0.0049	0.0209	0.0110	0.0061	0.0880	43.2
0.0360	0.0063	0.0269	0.0183	0.0101	0.1260	42.4

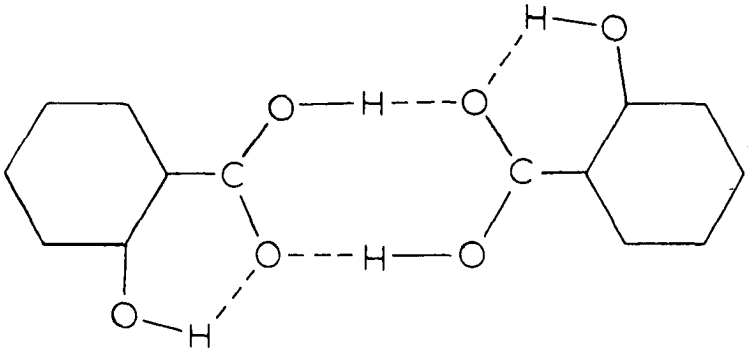
bution and solubility experiments clearly demonstrate the occurrence of hydration in the benzoic and salicylic acid systems. Dimerization constants and monomer distribution constants calculated from distribution data without regard to hydration are unquestionably in error. To illustrate, values of K_{20} can be determined for each system by the technique described by Almquist (22). According to equation 9 in Chapter I, the apparent value of K_{20} is related to the slope and intercept of the f_A/C_A^W versus C_A^W plot by K_{20} = slope/2 x $(\text{intercept})^2$. The least squares slopes and intercepts given in Table VI yield the following apparent dimerization constants: 190 l./mole for benzoic acid in benzene, 431 l./mole for salicylic acid in carbon tetrachloride, 27.1 l./mole for salicylic acid in benzene, and 5.9 l./mole for salicylic acid in ethylene dichloride. As expected, all of these values are notably smaller than the dimerization constants determined in the present study. Since the dimerization constant obtained by method B for the benzoic acid-benzene system is apparently still too low, the reliability of the K_{20} values for the salicylic acid systems might be questioned. However, it has been pointed out that additional data (water and acid solubility) were utilized in determining the five equilibrium constants for the

salicylic acid-benzene and salicylic acid-ethylene dichloride systems. Therefore, it is reasonable to suppose that five parameters could be determined with greater certainty from the data for these two systems.

Values of the hydration constants inferred from this study are believed to be reasonable. Previous hydration studies by Christian and co-workers (8,9,66,86,87) have shown that other polar solutes form monohydrates in organic solvents, and the association constants are within the range of the K_{11} values determined in this research. The values of K_{12} and K_{21} for the benzoic acid-benzene system seem to be compatible with $K_{12} = 483 \pm 21$ $1.^2/mole^2$ and $K_{21} = 890 \pm 55$ $1.^2/mole^2$ reported by Wood, et al. for the benzoic acid-diphenylmethane system (60). If the solubility of water in a solvent is considered an approximate measure of solvent reactivity, then benzene (water solubility at 25°C; 0.0349 mole/l. (71)) is a more reactive solvent than diphenylmethane (water solubility at 25°C; 0.0295 mole/l. (88)). Hence, the hydration constants for benzoic acid should be smaller for benzene than for diphenylmethane solutions. It appears after comparing results of method A and method B for the benzoic acid-benzene system that the determined values of K_{12} and K_{21} are relatively insensitive to the value of the

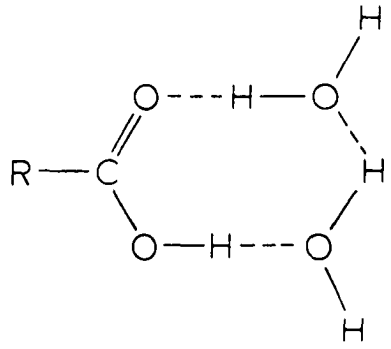
dimerization constant. Therefore, it is felt that the absolute errors in these hydration constants are small.

Obviously, definite conclusions concerning structures of the associated species cannot be drawn from the results of the distribution and solubility experiments. It has been commonly assumed that the anhydrous carboxylic acid dimer is predominantly cyclic in dilute solutions of non-polar solvents (10). Recent infrared absorption studies have indicated that cyclic dimerization is the most important association process in carbon tetrachloride solutions below acid concentrations of 4×10^{-3} mole/l. but that linear dimerization becomes significant at higher concentrations (12,52). Pauling has proposed the following structure for the salicylic acid dimer in nonpolar solutions;



in which all OH groups are involved in hydrogen bond formation (89). This structure has been confirmed in the crystal state by x-ray diffraction studies (90,91). It is reasonable that such a structure could also exist in non-

polar solvents. The structure of the monomer dihydrate species, AW_2, is also of interest. Statistically, AW_2 would not be expected to reach concentrations comparable to the monomer monohydrate species, AW. Results of this study indicate that AW_2 is at least as important in each system as AW. Christian, et al. have proposed a cyclic dihydrate structure,



to account for the apparent stabilization of the benzoic acid monomer dihydrate in diphenylmethane (60) and the trifluoroacetic acid monomer dihydrate in the vapor phase (92).

Effect of Solvent on the Dimerization of Salicylic Acid

A technique has been developed recently by Christian and co-workers which makes it possible to predict the effect of solvation on the thermodynamics of association reactions (93,94,95,96). For a typical association reaction,

donor (D) + acceptor (A) $\rightleftarrows$ complex (DA),

a dimensionless parameter, α, is defined by

$$\alpha = \frac{\Delta E^{o}_{DA}}{\Delta E^{o}_{D} + \Delta E^{o}_{A}} \qquad (45)$$

in which the ΔE^{o} terms refer to the changes in internal energy for the transfer of one mole of a species (D,A or DA) from the infinitely dilute solution (s) to the ideal vapor phase (v). α, defined in this way, represents the fraction of the internal energy of solvation of the monomers (D and A) that is retained by the complex (DA). Since complex formation is expected to "squeeze out" solvent molecules from the reactive sites of the monomers, the value of α should ordinarily be less than unity. This has been found to be the case for several hydrogen bonding reactions involving pyridine and water (87,93), aliphatic amines and water (9), and dimerization of trifluoroacetic acid (94). However, it has been found that α is greater than unity for certain types of association reactions. For example, if a particular complex is much more polar than the monomers from which it forms, the interaction between solvent and dipole of the complex may more than compensate for the "squeezing out" effect. This behavior has been noted for the highly polar 1:1 charge-transfer complex between SO_2 and trimethylamine, for which

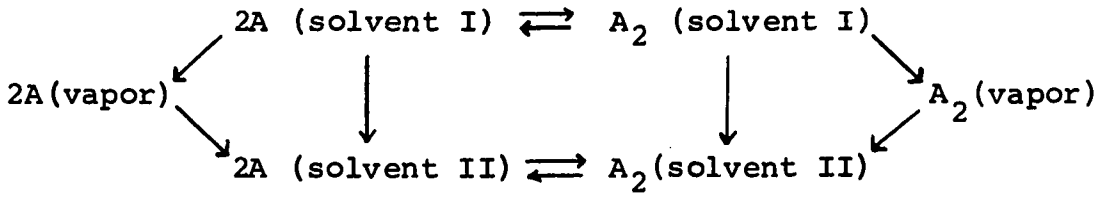
α is approximately 1.30 (95).

An equation analogous to equation 45 may be used to relate the Gibbs free energies of solvation of D, A and DA; i.e.,

$$\alpha' = \frac{\Delta G^{\circ}_{DA,\ s\rightarrow v}}{\Delta G^{\circ}_{D,\ s\rightarrow v} + \Delta G^{\circ}_{A,\ s\rightarrow v}} \qquad (46)$$

where standard states of 1 mole/l. (ideal dilute solution) are used for each species in both the vapor and liquid phase. It has been proposed that α (and also α') is not strongly dependent on temperature (93). In the limit of absolute zero temperature, α and α' must be equal since equations 45 and 46 become identical at $0^{\circ}K$. Furthermore, the two parameters are also expected to be approximately equal at low temperatures (96), and both are referred to hereafter as α.

If the value of α for a particular association reaction is known, it is possible to predict changes in the thermodynamic properties of the reaction for changes in the medium. For example, the effect of change of solvent on the dimerization of salicylic acid can be illustrated by the cycle,



It can be seen that the transfer from solvent I to solvent II can be accomplished by directly transferring the species between the solvents or by considering the vapor phase as an intermediate state. The change in Gibb's free energy for the dimerization reaction in going from solvent I to solvent II is given by

$$\Delta(\Delta G^{\circ})_{I\rightarrow II} = \Delta G^{\circ}_{A_2,\ I\rightarrow II} - 2\Delta G^{\circ}_{A,\ I\rightarrow II} \quad . \tag{47}$$

By transferring the dimer, A_2, through the vapor phase (v), this becomes

$$\Delta(\Delta G^{\circ})_{I\rightarrow II} = \Delta G^{\circ}_{A_2,\ I\rightarrow v} + \Delta G^{\circ}_{A_2,\ v\rightarrow II} - 2\Delta G^{\circ}_{A,\ I\rightarrow II} \quad . \tag{48}$$

Since α for the dimerization reaction is given by (see equation 46)

$$\alpha = \frac{\Delta G^{\circ}_{A_2,\ s\rightarrow v}}{2\Delta G^{\circ}_{A,\ s\rightarrow v}} \tag{49}$$

equation 48 may be expressed in terms involving only the free energies of the monomer;

$$\underset{I\rightarrow II}{\Delta(\Delta G^{o})} = 2\alpha_{I}\ \underset{I\rightarrow v}{\Delta G_{A}^{o}} - 2\alpha_{II}\underset{II\rightarrow v}{\Delta G_{A}^{o}} - 2\underset{I\rightarrow II}{\Delta G_{A}^{o}}. \qquad (50)$$

Equation 50 can be converted to a more convenient form by both adding and subtracting $2\alpha_{I}\underset{v\rightarrow II}{\Delta G_{A}^{o}}$ and rearranging to give

$$\underset{I\rightarrow II}{\Delta(\Delta G^{o})} = 2(\alpha_{I} - 1)\underset{I\rightarrow II}{\Delta G_{A}^{o}} + 2(\alpha_{II} - \alpha_{I})\underset{v\rightarrow II}{\Delta G_{A}^{o}}. \qquad (51)$$

It has been assumed in previous applications that the α parameter is very nearly independent of the choice of solvent (9,87,93). For situations in which this assumption is valid, the problem is simplified since the second term of equation 51 disappears. However, the value of α for the dimerization of salicylic acid is apparently not independent of the choice of solvent. Therefore, the second term of equation 51, which is effectively a correction term, must be considered in the present application.

Use of equation 51 requires knowledge of α values for the dimerization reaction in solvent I and solvent II and also the free energy changes $\underset{I\rightarrow II}{\Delta G_{A}^{o}}$ and $\underset{v\rightarrow II}{\Delta G_{A}^{o}}$. It is possible to estimate α values by a lattice treatment described by Stevens (94) following the method of Goates, et al. (97). If the salicylic acid dimer is considered

to have the structure illustrated on page 106, then the dimer should have 28 reactive sites to interact with the solvent (20 aromatic sites and 8 etheric oxygen lone-pair electrons). The energy required to transfer a dimer molecule from the ideal dilute solution (say carbon tetrachloride) to the ideal vapor phase is then given by

$$\Delta E^{\circ}_{A_2} = 20\epsilon_{H\text{-}Cl} + 8\epsilon_{OCl} - 14\epsilon_{ClCl}$$
$$CCl_4 \rightarrow v$$

where $20\epsilon_{H\text{-}Cl}$ (aromatic-solvent interactions) and $8\epsilon_{OCl}$ (etheric oxygen-solvent interactions) represent the energy required to remove a dimer molecule from solution, and $14\epsilon_{ClCl}$ (solvent-solvent interactions) represents the energy regained as the "cavity" left in the liquid collapses (94). Similarly, if the salicylic acid monomer is considered to retain the intramolecular hydrogen bond to the carbonyl oxygen, the monomer should have 16 sites for solvation (10 aromatic, 4 etheric oxygen, 1 keto oxygen, and 1 hydroxyl group). The energy of vaporization of the monomer from carbon tetrachloride is therefore,

$$\Delta E^{\circ}_{A} = 10\epsilon_{H\text{-}Cl} + 4\epsilon_{OCl} + \epsilon_{O\text{-}Cl} + \epsilon_{OHCl} - 8\epsilon_{ClCl}$$
$$CCl_4 \rightarrow v$$

where the additional terms $\epsilon_{O'Cl}$ and ϵ_{OHCl} represent keto oxygen-solvent and hydroxyl hydrogen-solvent interactions, respectively. Values of the individual group interaction energies, ϵ_{ij}, have been estimated from heat of vaporization and heat of mixing data and tabulated by Stevens (94). The appropriate group interaction energies yield the following energies of vaporization for the salicylic acid monomer and dimer (from carbon tetrachloride):

$$\Delta E_A^o = [10(1.22) + 4(1.50) + 2.43 + 2.00 - 8(1.22)] \frac{\text{kcal}}{\text{mole}}$$

$$\Delta E_{A}^{o}{}_{CCl_4 \rightarrow v} = 12.87 \text{ kcal/mole}$$

$$\Delta E_{A_2}^o = [20(1.22) + 8(1.50) - 14(1.22)] \text{ kcal/mole}$$

$$\Delta E_{A_2}^{o}{}_{CCl_4 \rightarrow v} = 19.32 \text{ kcal/mole} \quad .$$

From these energies, the value of α for the dimerization of salicylic acid in carbon tetrachloride can be determined.

$$\alpha_{CCl_4} = \frac{\Delta E_{A_2}^{o}{}_{CCl_4 \rightarrow v}}{2\Delta E_{A}^{o}{}_{CCl_4 \rightarrow v}} = \frac{19.32 \text{ kcal/mole}}{2(12.87) \text{ kcal/mole}} = 0.75$$

In a similar manner, energies of vaporization and α values can be determined for the solvents, benzene and ethylene dichloride. The latter solvent represents a more

difficult application of the lattice treatment since each solvent molecule possesses two different reactive sites, and the group interaction energies were derived from solvents with only one site. Stevens (94) has suggested taking the arithmetic mean of the individual group interaction energies; i.e., the interaction energy between a site on a solute molecule (S) and ethylene dichloride (E) can be found from $\epsilon_{SE} = \frac{2}{5}\epsilon_{SH} + \frac{3}{5}\epsilon_{SCl}$ (each chlorine atom in $C_2H_4Cl_2$ is assigned 3 sites and each hydrogen atom 1 site). Based on this reasoning, the calculated energies of vaporization and α for ethylene dichloride are:

$$\Delta E^{o}_{A_{C_2H_4Cl_2 \to v}} = 10.87 \text{ kcal/mole}, \qquad \Delta E^{o}_{A_{2\ C_2H_4Cl_2 \to v}} = 15.98 \text{ kcal/mole}$$

and $\alpha = 0.73$

Corresponding values for benzene are:

$$\Delta E^{o}_{A_{C_6H_6 \to v}} = 13.52 \text{ kcal/mole}, \qquad \Delta E^{o}_{A_{2\ C_6H_6 \to v}} = 18.32 \text{ kcal/mole}$$

and $\alpha = 0.68$

It is also possible to estimate the free energy changes required by equation 51. Christian and Grundnes (96) have shown by considering gas solubility data for a variety of solutes in nonpolar and slightly polar solvents (98,99) that $\Delta E^{o}_{i\ v \to s}$ and $\Delta G^{o}_{i\ v \to s}$ appear to be linearly related for various solutes (i) in a given solvent (s). For the 1 mole/l.

standard states, the gas solubility data for each solvent may be represented by

$$\underset{v \rightarrow s}{\Delta G_i^o} = \beta \underset{v \rightarrow s}{\Delta E_i^o} + 0.75\ RT \qquad (52)$$

where the parameter, β, is characteristic of the solvent only. Therefore, equation 52 provides a means for determining free energies of solvation from internal energy changes which have already been evaluated by the lattice method. The change in free energy for transfer of the monomer between solvent I and solvent II, $\underset{I \rightarrow II}{\Delta G_A^o}$, can be determined from the distribution constants given in Table XIV.

To illustrate the use of the treatment which has been described, let us consider the solvation effect on the dimerization of salicylic acid as the solvent is changed from C_6H_6 (I) to CCl_4 (II). Values of α for the dimerization reaction in these solvents have already been calculated. The change in free energy for transferring the monomer from the vapor to infinitely dilute CCl_4 solution is found by using equation 52 (β equals 0.64 for CCl_4 (96)) and the corresponding internal energy change (calculated by the lattice method); i.e.,

$$\underset{v \rightarrow CCl_4}{\Delta G_A^o} = (0.64)(-12.87 \text{ kcal/mole}) + 0.45 \text{ kcal/mole}$$
$$= -7.79 \text{ kcal/mole}.$$

The change in free energy for transferring the monomer from infinitely dilute C_6H_6 solution to infinitely dilute CCl_4 solution may be calculated from

$$\Delta G^{o}_{A,\ C_6H_6 \rightarrow CCl_4} = - RT \ln K_{D,A,\ C_6H_6 \rightarrow CCl_4} \qquad (53)$$

where the distribution ratio is given in terms of the monomer distribution constants in Table XIV:

$$K_{D,A,\ C_6H_6 \rightarrow CCl_4} = \frac{K_D^{CCl_4}}{K_D^{C_6H_6}} = \frac{0.352}{1.32} = 0.267 \ .$$

Substitution into equation 51 yields the following results:

$$\Delta(\Delta G^{o})_{C_6H_6 \rightarrow CCl_4} = [(2)(0.68-1)(-1.37 \log 0.267) + (2)(0.75-0.68)(-7.79)] \text{ kcal/mole}$$

$$= [-0.51-1.09] \text{ kcal/mole} = -1.60 \text{ kcal/mole} \ .$$

The predicted ratio in dimerization constants can be determined in the following way:

$$\log (K_{20}^{CCl_4}/K_{20}^{C_6H_6}) = -(1/2.3RT) \times \Delta(\Delta G^{o})_{C_6H_6 \rightarrow CCl_4}$$

$$= 1.60/1.37 = 1.16$$

$$K_{20}^{CCl_4}/K_{20}^{C_6H_6} = 14 \ .$$

It is interesting that the predicted ratio compares well with the observed ratio, 11.

In the same manner, a predicted ratio can be determined for changing the solvent from $C_2H_4Cl_2$(I) to CCl_4(II).

$$\Delta(\Delta G^{o})_{C_2H_4Cl_2 \rightarrow CCl_4} = [(2)(0.73-1)(-1.37 \log \{0.352/2.90\}) + (2)(0.75-0.73)(-7.79)] \text{ kcal/mole}$$

$$= [-0.68-0.31] \text{ kcal/mole} = -0.99 \text{ kcal/mole}$$

$$\log (K_{20}^{CCl_4}/K_{20}^{C_2H_4Cl_2}) = 0.99/1.37 = 0.72$$

$$K_{20}^{CCl_4}/K_{20}^{C_2H_4Cl_2} = 5$$

The predicted ratio in this case is in poor agreement with the observed ratio, 45.

The present application suggests that the method of Christian, et al. (93,94,96) is satisfactory for predicting solvation effects for the solvents carbon tetrachloride and benzene, but not for ethylene dichloride. It is felt that the failure encountered in dealing with the latter solvent arises mainly in evaluating the parameter, α. Since specific interactions between solute species and the solvent are apt to become increasingly important as solvent reactivity increases, it is expected that α should vary somewhat with solvent reactivity. Furthermore, the value of α for the dimerization process should presumably decrease with increasing solvent reactivity, since the monomer has relatively

more polar sites to be affected than does the dimer. The relative magnitudes of α as determined by the lattice method, 0.75 for CCl_4 and 0.68 for C_6H_6, are consistent with this reasoning. The value determined for $C_2H_4Cl_2$, 0.73, is apparently too high. In order to correlate satisfactorily the observed solvation effects, the value of α for the dimerization reaction in $C_2H_4Cl_2$ (estimated from equation 51) would have to be approximately 0.63. This hypothetical value is definitely more reasonable than 0.73 in comparison with the α -values for C_6H_6 and CCl_4.

Failure of the lattice method in yielding the α parameter in $C_2H_4Cl_2$ is undoubtedly due to the statistical nature of the treatment. The group interaction energies compiled by Stevens (94) and also the method which has been used to obtain α from the interaction energies are based upon the assumption that solute-solvent and solvent-solvent interactions are entirely non-specific. It is reasonable to believe that certain specific groups on either the monomer or the dimer of salicylic acid solvate preferentially in ethylene dichloride. For instance, the hydrogen atoms of $C_2H_4Cl_2$ are likely to be considerably more acidic than the hydrogen atoms of alkanes, upon which the group interaction energies are based. Consequently, the reactive oxygen sites

of the monomer and dimer could be expected to solvate preferentially via hydrogen-bonding to the solvent hydrogens, so that there would be more O---H interactions than the number predicted statistically.

Vapor Pressure Lowering Results

It has been established that hydration can be studied more effectively by distribution and solubility techniques when the extent of acid self-association is known. Unlike the case of the benzoic acid-benzene system, a study of the self-association of salicylic acid in the organic solvents by infrared spectroscopy does not appear feasible since difficulty would arise in unambiguously assigning measurable band intensities to either the monomer or dimer species. This leaves essentially the colligative properties from which to determine the extent of self-association of salicylic acid in the nonpolar solvents. Vapor pressure lowering (VPL) experiments are suitable in theory but have been limited in practice by the methods used in measuring pressures. However, greater precision in vapor pressure measurements is now available through recent developments in pressure measuring devices. VPL measurements for the acid systems have been determined with the aid of the very sensitive Texas Instrument Pressure Gage in an effort to

establish quantitatively the extent of self-association of the acids in the dry systems.

The apparent degree of self-association for each acid system can be approximated by comparing the VPL data and the calculated standard curves in Figures XII through XV. Although the data for each system are consistent with monomer-dimer equilibrium, a considerably higher degree of association is indicated in each case than has been implied by the distribution and solubility data. Since the VPL data also do not agree with the dimerization constant which has been considered reliable for the benzoic acid-benzene system at 25°C (589 l./mole), it is assumed that a systematic error has prevailed in measurements of the pressure differential, ΔP. The nature of the error has not yet been determined.

Disregarding the apparent systematic error, the VPL method would still not be an accurate technique for determining dimerization constants of highly associated acids. This can be seen by observing the data plots for the benzoic acid-benzene and salicylic acid-carbon tetrachloride systems (Figures XII and XIII). For systems of this type, the acid is nearly all dimer at concentrations necessary for significant vapor pressure lowering. As a result, no unique

value of the dimerization constant can be determined from the VPL data. VPL data become increasingly useful for determining association constants as the degree of association decreases. It can be seen that the data in Figure XIV for the salicylic acid-benzene system and the data in Figure XV for the salicylic acid-ethylene dichloride system approximately fit the lines calculated from dimerization constants of 180 l./mole and 45 l./mole, respectively. The VPL technique would be most ideally suited for studying the self-association of substances having even lesser tendencies to associate. For example, for a substance having a dimerization constant in benzene of say 10 l./mole, the monomer and dimer concentrations would be equal (0.1 mole/l.) at a total acid concentration, f_A, of 0.3 mole/l. The corresponding pressure differential, ΔP, theoretically would be 1.7 mm Hg. ΔP values of this magnitude could certainly be measured with far greater accuracy than the small values of ΔP encountered in the present study.

Summary

Distribution and solubility data have been collected at 25°C for the systems: benzoic acid-benzene, salicylic acid-carbon tetrachloride, salicylic acid-benzene, and

salicylic acid-ethylene dichloride. These data have been interpreted in terms of molecular association equilibria involving acid and dissolved water. Acid dimerization is the most significant association process taking place in each system, but hydration processes are also important. Monomer monohydrate, monomer dihydrate, and dimer monohydrate species must be considered together with anhydrous acid monomer and anhydrous acid dimer in order to explain satisfactorily all the data. Reasonable values of the association constants, monomer distribution constant, and standard errors in each constant have been inferred from nonlinear least squares analysis of the data for each system and are tabulated in Table XIII and Table XIV.

The results of this study prove that the interpretation of distribution data is much more complicated that has previously been assumed. Dimerization constants obtained in this study are considerably larger than corresponding values calculated from the data by the erroneous technique which has been commonly used in the past. Attempts to determine the acid dimerization constant for each of the systems by vapor pressure lowering measurements on dry solutions have not been successful. Although the VPL data are consistent with monomer-dimer equilibrium, the indicated degree of self-

association is apparently too high for each system. This behavior has been attributed to a systematic error in the measurements.

It has been found that intramolecular hydrogen bonding seemingly affects both dimerization and hydration of salicylic acid in organic solvents. The effect in general appears to be that intramolecular hydrogen bonding decreases the extent of intermolecular hydrogen bonding.

The effect of solvent upon the hydrogen bonding properties of salicylic acid is seen in two aspects of this study. First, it has been noted as expected that the magnitude of each association constant decreases with increasing solvent reactivity. Secondly, the percentage of the total amount of acid which is hydrated has been seen to increase with increasing solvent reactivity. This behavior is a result of the greater solubility of water in the more reactive solvents, which increases the importance of mass action in the hydration processes.

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